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Field Guide to

Light–Matter Interaction

Galina Nemova

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Introduction to the Series

2022 is a landmark year for the SPIE *Field Guide* series. It is our 19th year of publishing *Field Guides*, which now includes more than 50 volumes, and we expect another four titles to publish this year. The series was conceived, created, and shaped by Professor John Greivenkamp from the University of Arizona. John came up with the idea of a 100-page handy reference guide for scientists and engineers. He wanted these books to be the type of reference that professionals would keep in their briefcases, on their lab bench, or even on their bedside table. The format of the series is unique: spiral-bound in a 5″ by 8″ format, the book lies flat on any page while you refer to it.

John was the author of the first volume, the seminal *Field Guide to Geometric Optics*. This book has been an astounding success, with nearly 8000 copies sold and more than 72,000 downloads from the SPIE Digital Library. It continues to be one of the strongest selling titles in the SPIE catalog, and it is the all-time best-selling book from SPIE Press. The subsequent several *Field Guides* were in key optical areas such as atmospheric optics, adaptive optics, lithography, and spectroscopy. As time went on, the series explored more specialized areas such as optomechanics, interferometry, and colorimetry. In 2019, John created a sub-series, the *Field Guide to Physics*, with volumes on solid state physics, quantum mechanics, and optoelectronics and photonics, and a fourth volume on electromagnetics to be published this year. All told, the series has generated more than $1.5 million in print sales and nearly 1 million downloads since eBooks were made available on the SPIE Digital Library in 2011.

John's impact on the profession through the *Field Guide* series is immense. Rival publishers speak to SPIE Press with envy over this golden nugget that we have, and this is all thanks to him. John was taken from us all to early, and to honor his contribution to the profession through this series, he is commemorated in the 2022 Field Guides.

We will miss John very much, but his legacy will go on for decades to come.

Vale John Greivenkamp!

J. Scott Tyo
Series Editor, SPIE Field Guides
Melbourne, Australia, March 2022

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Preface

The interaction of light and matter has been a subject of scientific research since the 5th century BC. Its investigation has resulted in the evolution from the ancient corpuscular theory to the wave theory and finally to the quantum theory. Application of the theoretical research on light–matter interaction has led to numerous scientific achievements, including lasers, optical trapping, and optical cooling, among others. Indeed, it has brought into existence the entire field of photonics.

The primary objective of *Field Guide to Light–Matter Interaction* is to provide an overview of the basic principles of light and matter interaction using classical, semiclassical, and quantum approaches. The book covers basic photonics concepts using classical electrodynamics. A vast majority of light–matter interaction problems can be treated to a high accuracy within the semiclassical theory, where atoms with quantized energy levels interact with classical electromagnetic fields. The concepts involved in these problems are all addressed. The book also considers the interaction of matter with quantized electromagnetic fields consisting of photons. This approach gives a complete account of light–matter interaction, explaining many effects (such as the photoelectric effect) that cannot be explained using classical electromagnetic fields. The book elucidates the interaction of electromagnetic waves with atoms, molecules, solids, and plasma. It also covers the main concepts of optical pressure.

Field Guide to Light–Matter Interaction can also serve as a complement to *Field Guide to Laser Cooling Methods*, published by SPIE Press in 2019.

I would like to thank SPIE Director of Publications Patrick Franzen and Field Guide Series Editor Scott Tyo for the opportunity to write a Field Guide for one of the most interesting areas of current scientific research. I also wish to thank the anonymous reviewers for their many useful suggestions and comments on the draft of this Field Guide.

Preface

Finally, I wish to thank SPIE Press Sr. Editor Dara Burrows for her help.

This book is dedicated to my mom, Albina.

Galina Nemova
March 2022

Glossary of Symbols and Acronyms

Fundamental Constants

$b = 2.897771955 \times 10^{-3}$ m · K	Wien's displacement constant
$c = 2.99793 \times 10^{8}$ m · s^{-1}	speed of light in vacuum
$e = -1.602176634 \times 10^{-19}$ C	electron charge
$h = 6.626 \times 10^{-34}$ J · s	Planck's constant
$\hbar = h/2\pi$	reduced Planck's constant
$m_e = 9.1096 \times 10^{-31}$ kg	mass of an electron
$\varepsilon_0 = 8.8541878128(13) \times 10^{-12}$ F · m^{-1}	vacuum permittivity
$\kappa_B = 1.380649 \times 10^{-23}$ J · K^{-1}	Boltzmann constant
$\mu_0 = 1.25663706212(19) \cdot 10^{-6}$ H · m^{-1}	vacuum permeability
$\mu_B = 0.927 \times 10^{-23}$ A · m^{-2}	Bohr magneton
$\sigma = 5.670373 \times 10^{-8}$ W · m^{-2} · K^{-4}	Stefan–Boltzmann (or Stefan's) constant

Units of Measure

A	ampere	kg	kilogram
C	coulomb	m	meter
F	farad	s	second
H	henry	T	tesla
J	joule	V	volt
K	kelvin	W	watt

Frequently Used Symbols

It is impossible to avoid using the same symbols for more than one quantity. A list of symbols denoting a single quantity is presented here. Other symbols are defined in the body of the book.

A	mass number
a_H	Bohr radius

Glossary of Symbols and Acronyms

$\vec{B}$	magnetic induction
$\vec{D}$	electric field displacement
$\vec{E}$	electric field strength
e	electron charge (a negative number)
g	degeneracy
$\vec{H}$	magnetic field strength
J	total angular momentum quantum number (for multi-electron atoms)
$\vec{J}$	total angular momentum (for multi-electron atoms)
j	total quantum number
$\vec{j}$	total angular momentum (for single-electron atoms)
$\tilde{j}$	surface current density
k	wave vector magnitude
$\vec{k}$	wave vector
k_0	vacuum wave vector magnitude ($k_0 = \omega/c$)
k_{sp}	spring constant
L	total orbital angular momentum quantum number (for multi-electron atoms)
$\vec{L}$	total orbital angular momentum (for multi-electron atoms)
l	orbital quantum number
$\vec{l}$	orbital angular momentum (for single-electron atoms)
l_l	longitudinal coherence length
l_t	transverse coherence length
m_l	magnetic quantum number
m_s	spin magnetic quantum number
N	neutron number
P	magnitude of the polarization vector ($P = \|\vec{P}\|$)
$\vec{P}$	polarization vector
p	photon momentum magnitude
r	radius
S	total spin quantum number (for multi-electron atoms)
$\vec{S}$	total electron spin (for multi-electron atoms)

Glossary of Symbols and Acronyms

s	spin quantum number
$\vec{s}$	spin (for single-electron atoms)
T	temperature
v	velocity
V_{coh}	coherence volume
Z	atomic or proton number
α	polarizability
Δ	detuning ($\Delta = \omega_0 - \omega$)
$\boldsymbol{\varepsilon}$	linear dielectric tensor
ε	dielectric permittivity
$\hat{\varepsilon}$	unit vector
λ	wavelength
μ	magnetic permeability
ν	frequency
ρ	density matrix
φ_p	phase angle
ω	angular frequency ($\omega = 2\pi\nu$)

Acronyms and Abbreviations

BCE	Before Common Era
c.c.	complex conjugate
CG	Clebsch–Gordon
CM	center of mass
DC	direct current
ED	electric dipole
EM	electromagnetic
FWHM	full width at half-maximum
h.c.	Hermitian conjugate
HWHM	half width at half-maximum
IR	infrared
LA	longitudinal acoustic
LO	longitudinal optical
LP	left polarization
MD	magnetic dipole
OPL	optical path length
RP	right polarization
RW	radio waves
RWA	rotating-wave approximation

Glossary of Symbols and Acronyms

RE	rare earth
SAM	spin angular momentum
SF	superfluorescence
SI	International System of Units
SPhP	surface phonon polariton
SR	superradiance
TA	transverse acoustic
TO	transverse optical
UV	ultraviolet

Light and Matter in Ancient Greece

The term light–matter interaction covers a wide variety of physical phenomena ranging from classical to quantum electrodynamics. It is relevant to black holes and neutron stars. To understand the topic, one needs to answer three questions: What is light? What is matter? What is the interacting agent providing the interaction?

The first theories of light–matter interaction were developed by pre-Socratic philosophers who were active during the 5th and 6th centuries BCE in Greece.

In c. 430 BCE, **Empedocles** (c. 490–430 BCE) proposed that the world is composed of four elements, or "roots"—fire (shining Zeus), air (life-bringing Hera), earth (Aidoneus), and water (Nestis). Empedocles taught that these immutable elements are both spiritual and physical; they produce the diversity and changes in the world by the influence of two forces, repulsion (strife) and attraction (love). He did not ascribe this emotional principle to any personified existence.

Speculating about light, Empedocles believed that Aphrodite made the human eye out of the four elements and that she lit the fire in the eye, which shone out from the eye, making sight possible.

Empedocles's idea concerning light was developed by **Euclid** (who flourished c. 300 BCE). Euclid assumed that the fire flux moved in straight lines, and he used the idea to explain some optical phenomena in his work *Optica*.

Leucippus (c. 480–420 BCE) proposed the theory of **atomism**, which was free from any traces of mythical and spiritual elements. He and **Democritus** (c. 460–370 BCE) thought that the universe comprises an infinite number of permanent, immutable, indivisible elements called **atoms** (from the Greek *atomon*, i.e., uncuttable, indivisible) and the empty space or **vacuum** (from the Latin adjective *vacuus* for vacant or void) through which the atoms move. In this ancient theory, atoms interact with each other mechanically. The theory of atomism is closer to modern science compared to any other theory of antiquity.

Light and Matter in the Common Era

Influenced by Euclid's *Optica,* Claudius **Ptolemy** (90–168 AD) developed geometrical astronomy, which was considered as definitive until the European Renaissance.

In 1637, René **Descartes** stated that light is made up of small, discrete particles called "**corpuscles**" (little particles) that travel in a straight line with a finite velocity.

In 1649, modern atomic theory was proposed by Pierre **Gassendi** (1592–1655). In his works *De Vita et Moribus Epicuri* and the *Syntagma Philosophiae Epicuriae*, Gassendi reviewed the doctrines of **Epicurus** (c. 342–270 BCE) who, in 306 BC, championed Democritus's atomic theory.

In 1801–1803, Thomas **Young** carried out experiments that proved the wave theory of light.

In 1861, James Clerk **Maxwell** predicted the existence of electromagnetic waves. Maxwell's equations clearly revealed the existence of such electromagnetic waves.

In 1897, Sir Joseph John **Thomson** discovered the electron.

In 1911, Ernst **Rutherford** discovered the atomic nucleus and established that the mass of the atom is concentrated in its nucleus.

In 1913, Niels **Bohr** proposed a model of an atom with a central nucleus surrounded by orbiting electrons.

In 1905, Albert **Einstein** proposed the quantization of radiation, which re-established the corpuscular properties of light. The dual nature of light as both a particle and a wave was proved. Its essential theory further evolved from electromagnetics into quantum mechanics.

In 1926, Erwin **Schrödinger** proposed a wave–mechanical model of the atom. He formulated a wave equation (the **Schrödinger equation**), which allows one to calculate the energy levels of electrons in atoms.

> Maxwell's theory of electrodynamics and quantum mechanics are the current basis for understanding light–matter interaction.

The Current Evolution of the Concept of Light

Controversies concerning the nature of light have a very long history.

In 1690, Christiaan **Huygens** published his book *Traité de la Lumière* [*Treatise on Light*], in which he proposed the wave theory of light.

In 1704, Sir Isaac **Newton** published *Opticks*, in which he presented his corpuscular theory of light. Newton's theory was predominant for more than 100 years. However, some scientists such as Leonard Euler, Mikhail Lomonosov, and Benjamin Franklin disagreed with Newton's corpuscular theory of light presented in *Opticks* and supported Huygens' wave theory of light.

In 1849–1850, Michel **Foucault** and Hippolyte **Fizeau** measured the speed of light. Their experiment showed that light travels more slowly through water than through air, a finding that could not be explained by Newton's corpuscular theory of light.

In 1865, James Clerk **Maxwell** published *A Dynamical Theory of the Electromagnetic Field*, where he demonstrated that electric and magnetic fields travel through space as waves moving at the speed of light.

In 1859, Gustav **Kirchhoff** experimentally investigated the intensity of the thermal electromagnetic radiation emitted by a blackbody. The classical theoretical treatment did not agree with his experimental results.

In 1900, Max **Planck** postulated that electromagnetic energy could be emitted only in quantized amounts (or packets) of energy (the **Planck postulate**). Thus, the quantum theory of light was born. Physicists now call these packets light **quanta** or **photons**.

Light propagation can be described with the **wave theory of light**. To understand the interaction between light and matter (on the atomic scale), the **quantum theory of light** must be used.

Maxwell's Equations

Maxwell's equations, which were proposed by Maxwell in 1865, describe the laws of the electromagnetic field. The fundamental laws, such as Ampere's law, Faraday's law, Coulomb's law, and the magnetic continuity law, were cast by Heaviside into four equations, which can be presented in integral and differential forms. In SI units, these are:

Integral form		Differential form
$\oint_L \vec{H} d\vec{l} = \int_S \left(\vec{j} + \frac{\partial \vec{D}}{\partial t}\right) d\vec{S}$	(**Ampere's law**)	$\nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}$
$\int_L \vec{E} d\vec{l} = -\int_S \frac{\partial \vec{B}}{\partial t} d\vec{S}$	(**Faraday's law**)	$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$
$\oint_{\tilde{S}} (\vec{D} d\vec{S}) = \int \rho dV$	(**Gauss's law**)	$\nabla \cdot \vec{D} = \rho$
$\oint_{\tilde{S}} (\vec{B} d\vec{S}) = 0$	(**no magnetic monopole**)	$\nabla \cdot \vec{B} = 0$

where $\vec{E}$ and $\vec{H}$ are the instantaneous electric field strength and magnetic field strength, respectively; $\vec{D}$ and $\vec{B}$ are the electric displacement vector and the magnetic induction vector, respectively; and $\vec{J}$ and ρ are the current and volume charge density, respectively. S is any surface that is bound by the closed curve L, and $\tilde{S}$ is a closed surface. Maxwell's equations form the basis for describing all electromagnetic phenomena. For macroscopic media, the dynamical response is summarized in the relations that connect $\vec{D}$ and $\vec{j}$ with $\vec{E}$, and $\vec{B}$ with $\vec{H}$, i.e.,

$$\vec{D} = \varepsilon \vec{E}, \quad \vec{j} = \sigma \vec{E}, \quad \text{and} \quad \vec{B} = \mu \vec{H}$$

respectively. ε is the **dielectric permittivity**, μ is the **magnetic permeability** of the medium, and σ is the **electrical conductivity**. In the case of vacuum (free space), $\varepsilon = \varepsilon_0$ and $\mu = \mu_0$. If the physical properties of the medium (characterized by ε and μ) change abruptly across a surface, Maxwell's equations in an integral form are valid for the structure. In this case, boundary conditions (see next page) need to be added to Maxwell's equations in their differential forms.

Boundary Conditions

For a medium with an abrupt change in its physical properties, the following relations hold (given in SI units):

- The normal components of the **electric displacement** (D_{2n} and D_{1n}) change abruptly across the surface by an amount equal to the surface charge density $\tilde{\rho}$:

$$D_{2n} - D_{1n} = \tilde{\rho}$$

- The normal components of the **magnetic induction** (B_{2n} and B_{1n}) are continuous across the surface:

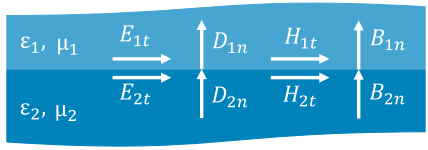
$$B_{2n} = B_{1n}$$

- The tangential components of the **electric field strength** (E_{2t} and E_{1t}) are continuous across the surface:

$$E_{2t} = E_{1t}$$

- The tangential components of the **magnetic field strength** (H_{2t} and H_{1t}) change abruptly by an amount equal to the surface current density $\tilde{j}$:

$$H_{2t} - H_{1t} = \tilde{j}$$



Consider a medium that is free of any abrupt changes in its physical properties. Assume that a source in this medium begins to radiate at any instant in time t_0. The disturbance will spread into the surrounding space. At any later instant in time, $t_1 > t_0$, a defined region of the medium will be filled with this disturbance. At the **boundary** of this region, the magnitudes of the field vectors will change abruptly from finite values on the boundary to zero outside the boundary.

Electromagnetic Waves

Maxwell's wave equations for vacuum are as follows:

$$\nabla \cdot \vec{E} = 0,\ \nabla \times \vec{E} = -\mu_0 \frac{d\vec{H}}{dt}, \quad \nabla \cdot \vec{H} = 0, \nabla \times \vec{H} = \varepsilon_0 \frac{d\vec{E}}{dt}$$

These equations can also be presented as

$$\nabla \times (\nabla \times \vec{E}) = -\mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}, \quad \nabla \times (\nabla \times \vec{H}) = -\mu_0 \varepsilon_0 \frac{\partial^2 \vec{H}}{\partial t^2}$$

Using the relation $\nabla \times (\nabla \times \vec{A}) = \nabla(\nabla \cdot \vec{A}) - \nabla^2 \vec{A}$, which is valid for any vector $\vec{A}$, one can obtain the wave equations for the electric field $\vec{E}$ and magnetic field $\vec{H}$, respectively, as

$$\nabla^2 \vec{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}, \quad \nabla^2 \vec{H} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{H}}{\partial t^2}$$

These wave equations have the same form: $\nabla^2 \vec{A} = \frac{1}{v^2} \frac{\partial^2 \vec{A}}{\partial t^2}$

The solution of this equation is an oscillatory wavefunction with an amplitude that is transverse to the direction of propagation. v is associated with the velocity of the wave. For wave propagation in the z direction, we use only the z component, $A_z(z,t)$, of $\vec{A}$. We assume that $A_z(z,t)$ can be presented as $A_z(z,t) = Z(z)T(t)$. In this case, the wave equation for $\vec{A}$ can be presented as

$$\frac{v^2}{Z}\frac{d^2 Z}{dz^2} = \frac{1}{T}\frac{d^2 T}{dt^2}$$

Both sides of the equation must equal the same constant, which can be denoted as $-\omega^2$. We now have two equations:

$$\frac{d^2 Z}{dz^2} + \frac{\omega^2}{v^2} Z = 0, \qquad \frac{d^2 T}{dt^2} + \omega^2 T = 0$$

which have as solutions $Z(z) \sim e^{\pm i(\omega/v)z}$ and $T(t) \sim e^{\pm i\omega t}$, respectively. A general solution can be presented in the following form:

$$A_z(z,t) \sim e^{-i[k_z z - \omega t]}, \text{ where } k_z = \frac{\omega}{v} \text{ is the } \textbf{wavenumber}.$$

Properties of Electromagnetic Waves

In a general form, the electric and magnetic field vectors of electromagnetic waves propagating in the $\vec{k}$ (**propagation vector**) direction can be expressed as

$$\vec{A}(x,y,z,t) = \vec{A}_0 e^{-i(\vec{k}\cdot\vec{r}-\omega t)}, \text{ where } \vec{A} \text{ is } \vec{E} \text{ or } \vec{B}$$

$$\nabla \cdot \vec{E} = 0 \rightarrow i\vec{k} \cdot \vec{E} = 0 \rightarrow \vec{E} \perp \vec{k}$$

$$\nabla \cdot \vec{H} = 0 \rightarrow i\vec{k} \cdot \vec{H} = 0 \rightarrow \vec{H} \perp \vec{k}$$

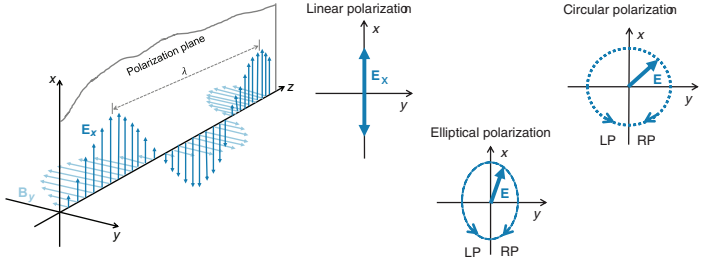
The electric field vector $\vec{E}$ and magnetic field vector $\vec{B}$ are perpendicular to $\vec{k}$ as well as to each other in an infinite, nonconducting, isotropic medium. Electromagnetic waves are **transverse waves**.

A wave traveling in the z direction can be presented as two orthogonal components (polarizations):

$$\vec{E} = E_{0x}\vec{i}e^{-i(k_z z-\omega t)} + E_{0y}\vec{j}e^{-i(k_z z-\omega t+\varphi_p)}$$

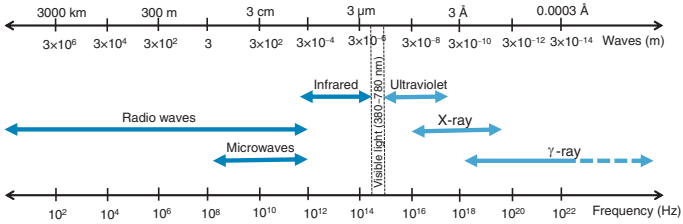
where $\vec{i}$ and $\vec{j}$ are unit vectors in the x and y directions, respectively, and φ_p is the phase angle.

- If $\varphi_p = \pm m\pi$, where m is an integer, we have **plane** or **linearly polarized light**.



- If $E_{0x} = E_{0y}$ and $\varphi_p = \pm(2\,m+1)\pi/2$, we have **circularly polarized light**, which can be right polarized (RP) or left polarized (LP); otherwise, the light is **elliptically polarized**.
- If φ_p *varies* in a random manner, we have **unpolarized light**.

The Electromagnetic Spectrum



Radio waves (RW) were predicted by Maxwell in 1867. Use of modulated RWs became possible for sending information over long distances.

Microwaves are the shortest-wavelength and highest-energy form of RWs. They are widespread in nature and are produced by a variety of astronomical processes.

Infrared (IR) is electromagnetic radiation with wavelengths slightly longer than the reddest visible light. The IR was discovered by William Herschel in 1800 and is known as **heat radiation**. All objects emit IR radiation according to their temperature and emissivity.

Visible light is the light that is visible to our eyes. It covers a very narrow range of wavelengths between 380 nm and 780 nm. In 1666, Newton proved that the white light from the Sun is a blend of different colors and wavelengths that can be separated with a prism.

Ultraviolet (UV) is electromagnetic radiation with wavelengths slightly shorter than visible light. The UV was discovered by Johann Wilhelm Ritter in 1801. UV radiation forms a substantial part of the Sun's radiation. It is largely blocked by ozone in Earth's atmosphere.

X-ray is high-energy radiation. X-rays were discovered by Wilhelm Röntgen in 1895. Many astronomical objects generate x-rays, but Earth's atmosphere provides an effective x-ray absorbing shield.

γ-ray is the shortest-wavelength and highest-energy radiation. γ-rays were discovered around the turn of the 20th century during investigation of radiative decay processes. Their extremely short wavelengths allow them to pass through many materials without interaction.

The distribution of energy across these spectral bands is governed by **Planck's law** (see page 11).

Cavity Radiation

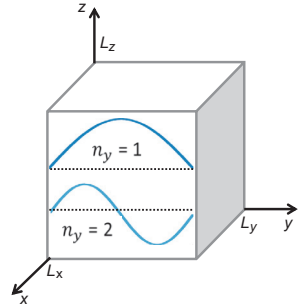
Standing waves within a rectangular cavity with dimensions L_x, L_y, L_z can be described by an **oscillatory function** $\mathrm{Re}\{\exp[-i(k_x x + k_y y + k_z z)]\}$. The field must be periodic in L and must be either null or a maximum at the boundaries of the cavity; i.e., $k_x L_x = n_x \pi$, $k_y L_y = n_y \pi$, and $k_z L_z = n_z \pi$, where $n_{x,y,z} = 0, 1, 2 \ldots$.

The propagation vector $\vec{k}$ must satisfy the relation

$$|\vec{k}|^2 = (k_x^2 + k_y^2 + k_z^2) = \left[\left(\frac{k_x \pi}{L_x}\right)^2 + \left(\frac{k_y \pi}{L_y}\right)^2 + \left(\frac{k_z \pi}{L_z}\right)^2\right]$$

$|\vec{k}| = \frac{2\pi}{\lambda}$, where λ is the wavelength.

The **number of modes** along $\vec{x}$, $\vec{y}$, and $\vec{z}$ are $n_x = 2L_x/\lambda$, $n_y = 2L_y/\lambda$, and $n_z = 2L_z/\lambda$, respectively. This consideration is valid for volumes greater than the wavelength λ.



The number of modes for frequencies up to the value ν within a volume $V = L_x L_y L_z$ is

$$N_{mode} = \frac{2}{8}\frac{4\pi}{3}\left(\frac{2L_x 2L_y 2L_z}{\lambda^3}\right) = \frac{8\pi}{3\lambda^3} V = \frac{8\pi\nu^3}{3c^3} V$$

Two orthogonal polarizations of the electromagnetic waves must be considered for each spatial mode.

The number of modes per unit volume is

$$\rho(\nu) = \frac{N_{mode}}{V} = \frac{8\pi\nu^3}{3c^3}$$

The number of modes per unit volume within a given frequency interval between ν and $\nu + d\nu$ is

$$\boxed{\frac{d\rho(\nu)}{d\nu} = \frac{8\pi\nu^2}{c^3}}$$

This relation is valid for any cavity shape.

The Stefan–Boltzmann Law

Any body whose temperature is above absolute zero (0 K) emits energy that is transferred by electromagnetic radiation (**radiant energy**) according to the **Stefan–Boltzmann law**:

$$\dot{Q} = \varepsilon\sigma A T^4$$

where $\dot{Q}$ is the radiant energy emission rate, ε is the **emissivity** (**relative emittance**), σ is the **Stefan–Boltzmann constant**, A is the surface area, and T is the absolute temperature. The emissivity is a dimensionless number ($0 < \varepsilon < 1$). The most effective radiators are surfaces for which $\varepsilon \to 1$ (blackbodies). Surfaces for which $\varepsilon \to 0$ (highly polished surfaces) reflect radiation rather than absorbing it. The transfer of energy by electromagnetic waves in the thermal range (0.1–100 μm) is known as **thermal radiation**.

In 1860, Kirchhoff proposed the theoretical concept of a perfect **blackbody**, which has $\varepsilon = 1$. Such an object might seem like a theoretical abstraction, but a metallic cavity with a small aperture can serve as a blackbody, which is both a perfect absorber and a perfect emitter of electromagnetic radiation. Its radiation emission is dependent only on its surface temperature. The equation for a blackbody spectrum was developed by Rayleigh and Jeans, who considered the behavior of electromagnetic waves within a cavity. Using $\kappa_B T$ as the value of the energy per mode, they obtained the relation (the **Rayleigh–Jeans formula**),

$$u(\nu) = \frac{d\rho(\nu)}{d\nu}\kappa_B T = \frac{8\pi\nu^2}{c^3}\kappa_B T$$

describing the spectral density of thermal radiation in classical physics. Here κ_B is the **Boltzmann constant**, c is the speed of light, and ν is the frequency. $u(\nu) \to \infty$ at high frequencies (the **ultraviolet catastrophe**); i.e., classical physics predicts a completely unreasonable result at high frequencies.

Planck's Law for Cavity Radiation

Planck questioned the assumption that a value $\kappa_B T$ can be used as the average energy per cavity mode. He postulated that an oscillator of frequency ν can have only discrete values $n_{osc}h\nu$ of energy, where $n_{osc} = 0, 1, 2, 3, \ldots$. He named the unit energy $h\nu$ a **quantum**, which cannot be further divided. In this case, the energy of each cavity mode in thermal equilibrium can be obtained using the **Boltzmann distribution** with energy $E_n = n_{osc}h\nu$. The distribution function is $f_n = Ce^{-n_{osc}h\nu/\kappa_B T}$. Accounting for the normalizing condition, one can obtain the relation for C:

$$\sum_{n_{osc}=0}^{\infty} f_{n_{osc}} = \sum_{n_{osc}=0}^{\infty} Ce^{-n_{osc}h\nu/\kappa_B T} = 1 \rightarrow C = 1 - e^{-h\nu/\kappa_B T}$$

The average mode energy of the oscillators is

$$\bar{E} = \frac{\sum_{n_{osc}=0}^{\infty} E_n f_n}{\sum_{n_{osc}}^{\infty} f_n} = \frac{h\nu}{e^{h\nu/\kappa_B T} - 1}$$

Planck replaced the $\kappa_B T$ value in the Rayleigh–Jeans formula with the average mode energy $\bar{E}$ and obtained the relationship for the energy density per unit frequency ν for radiation within an enclosed cavity in thermal equilibrium at temperature T as follows (**Planck's formula**):

$$u(\nu) = \frac{8\pi h\nu^3}{c^3(e^{h\nu/\kappa_B T} - 1)}$$

where h is **Planck's constant**. This formula was presented on 14 December 1900 (the "birthday" of quantum physics).

The total energy density is

$$u = \int_0^{\infty} u(\nu)d\nu = \frac{8}{15}\frac{\pi^5 \kappa_B^4}{c^3 h^3} T^4$$

In this formula, the following relation is used:

$$\int_0^{\infty} \frac{x^3 e^{-x}}{1 - e^{-x}} dx = \int_0^{\infty} x^3 e^{-x}(1 + e^{-x} + e^{-2x} + \ldots)dx = \frac{\pi^4}{15}$$

Blackbody Radiation

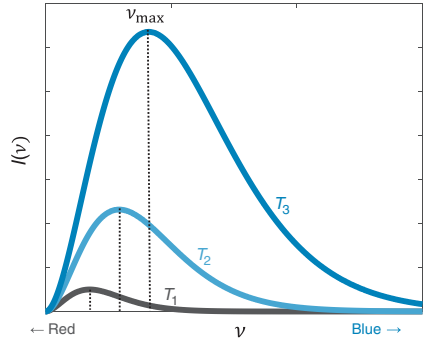
If one makes a small hole in a cavity, a beam of intensity $I(\nu)$ at any frequency ν will emerge from the hole. The observed Planck **blackbody radiation** is

$$I(\nu) = cu(\nu) = \frac{8\pi h\nu^3}{c^2(e^{h\nu/\kappa_B T} - 1)}$$

The Rayleigh–Jeans blackbody radiation equation is

$$I_{RJ}(\nu) = \frac{8\pi h\nu^3}{c^2}\kappa_B T$$

The maximum of Planck's intensity occurs at the frequency ν_{max}, which increases with temperature T ($T_1 < T_2 < T_3$). It was discovered experimentally that $\nu_{max} \sim T$ (**Wien's displacement law**). This frequency displacement is responsible for the changes in the color of a solid with temperature. Wien's displacement law can be presented as $\lambda_{max} T = b$, where $\lambda_{max} = c/\nu_{max}$, and b is **Wien's displacement constant**.



The radiant energy emission rate per unit area of a blackbody is

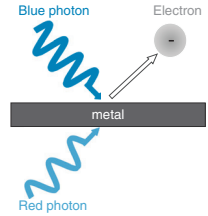
$$\dot{\tilde{Q}}_{bb} = \pi I = \sigma T^4$$

where $I = \int_0^\infty I(\nu)d\nu$, and $\sigma = \frac{2\pi\kappa_B^4}{15c^2\hbar^2}$ is the relation for the **Stefan–Boltzmann constant**.

The Photon

In 1900, Planck postulated that radiation emission and absorption by matter can occur only in discrete amounts (energy quanta). He believed that light propagating in free space can be described by Maxwell's equations.

At the turn of the 20th century, the emission of electrons from the surface of some metals that were exposed to certain frequencies of light was observed. When red light illuminated a surface, the surface remained unaffected, but even weak blue light caused the emission of electrons (the **photoelectric effect**) from the metal surface.



In 1905, Einstein postulated that light propagating in free space can be treated as a stream of particles (energy quanta or **photons**) whose energy depends on their frequency ν as $E = h\nu$. This means that intense red light merely delivers large quantities of lower-energy photons that are not sufficient to overcome the binding energy of an electron at the surface. The **photon energy** can also be presented as

$$E = h\nu = \hbar\omega = hc/\lambda$$

where $\hbar = h/2\pi$ is the **reduced Planck constant**, ω is the angular frequency, and λ is the wavelength. The photon has a linear **photon momentum** of magnitude

$$p = h\nu/c = \hbar k = h/\lambda$$

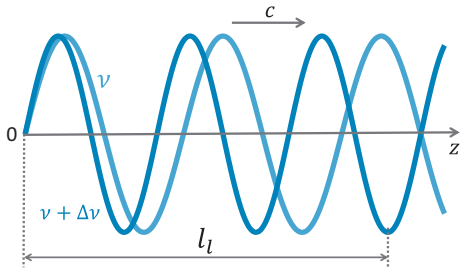
where $k = |\vec{k}| = 2\pi/\lambda$ is the magnitude of the wave vector $\vec{k}$. The photon travels in free space at the speed of light c and has zero rest mass. It has a **spin angular momentum** (SAM) of $\pm\hbar$, where the $+$ and $-$ signs correspond to left- and right-circularly polarized light in space, respectively. The SAM is directed along the beam propagation direction, z. Photons are bosons.

Temporal and Spatial Coherence

Temporal (**longitudinal**) **coherence** describes the relative phase of two waves along their propagation direction. Consider two waves propagating along z with the frequencies ν and $(\nu + \Delta\nu)$ at the speed of light c. We assume that these two waves are in phase at $z = 0$. After the length of time $\delta_\tau = 1/\Delta\nu$ (the **coherence time**), these two waves will be out of phase. The length

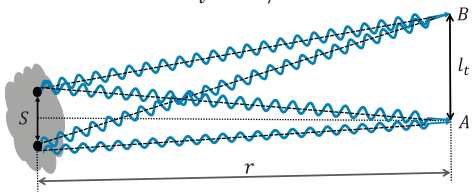
$$l_l = c\delta_\tau = c/\Delta\nu = \lambda^2/\Delta\lambda$$

is the **longitudinal coherence length**. Here, $\Delta\lambda$ is the wavelength difference between the two waves, and λ is their average wavelength. The coherence length has a significant value only when $\Delta\lambda < \lambda$, i.e., when the wavelengths of both waves are nearly identical.



Spatial (**transverse** or **lateral**) **coherence** describes how far apart two points radiating at frequency $\nu = c/\lambda$ can be located and still exhibit coherent properties. Consider the two light sources separated by a distance S. A is the point where these two sources manifest interference. B is the point where interference disappears. The distance between A and B is known as the **transverse coherence length**:

$$l_t = r\lambda/S$$

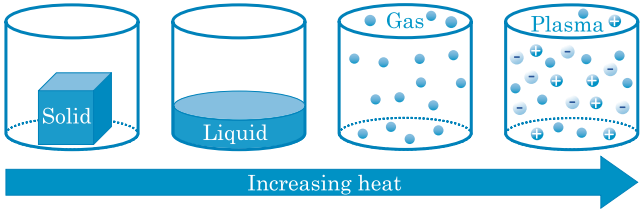


The value $V_{coh} = \pi \frac{c}{\Delta\nu} \frac{r^2\lambda^2}{S^2}$ is the **coherence volume**.

Matter

Matter is a collection of nonrelativistic particles that forms plasma, liquids, gases, and solids, known as the **four main states of matter**. Matter has mass and takes up space.

Many substances can be transformed from one of these four states to another of these states when the temperatures of the substances are changed by either adding or removing energy from the system.



In **solids**, atoms and molecules are tightly bound together by strong interatomic bonds and weaker intermolecular bonds. The particles tend to arrange themselves in regular long-scale crystalline structures. In solids, atoms and molecules are held firmly in place. They can vibrate within a limited area but cannot move through the structure.

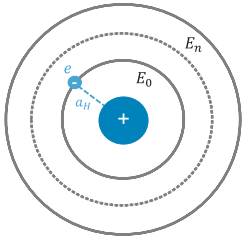
In **liquids**, atoms and molecules are still very close together, but the bonds between them are weaker than in solids. The atoms and molecules that form liquids flow around one another, but attractive forces between them keep them from flying apart. A liquid maintains its volume but takes the shape of its container.

In **gases**, the bonds linking individual atoms and molecules are broken. The forces acting between particles are nearly negligible. Interactions between particles in gases are weak compared to their thermal motions and are dominated by binary collisions. A gas has no fixed shape; it completely fills its container.

Plasma is an ionized gas or another medium in which charged particles interact with each other. Plasma's behavior is determined by a collective interaction through the electromagnetic fields of its charged particles.

The Bohr Theory of the Hydrogen Atom

In 1885, Johann Jakob Balmer introduced the relation $\lambda = bn^2/(n^2-4)$ (the **Balmer formula**), which can explain the hydrogen spectrum. Here, λ is the wavelength, $b = 3645.6$, and $n = 3,4,5,6$. Unfortunately, the Balmer formula cannot be applied to any other elements, nor can it even be applied to all wavelengths emitted by hydrogen.



Approximately 30 years later, Niels Bohr proposed a model of the **hydrogen atom** that not only explained the Balmer formula, but also gave a new view of the atomic structure. He assumed that almost all of the mass of a hydrogen atom is concentrated in the charged nucleus. In the Bohr model, the electron, which travels in a circular orbit about the nucleus, is attracted to the nucleus by the Coulomb force law. The magnitude of this force is $F = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}$. Bohr assumed the validity of Newton's laws of motion for the orbit and calculated a centripetal acceleration of the electron as $a = \frac{v^2}{r}$. From Newton's second law of motion, $\vec{F} = m_e\vec{a}$, we have: $\frac{m_e v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}$. The electron's kinetic and potential energies are $T_{kin} = \frac{m_e v^2}{2}$ and $V_{pot} = -\frac{e^2}{4\pi\varepsilon_0 r}$, respectively. $E_{tot} = T_{kin} + V_{pot} = -\frac{e^2}{8\pi\varepsilon_0 r}$ is the electron's total energy. Bohr postulated that only orbits that permit the electron's angular momentum $L = nh/2\pi$ can be used by the electron. Here, $n = 1,2,3,\ldots$, and h is the Planck constant. The angular momentum for a circular orbit is $L = m_e v r$. In this case, the allowed energies of a hydrogen electron are $\boxed{E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{E_0}{n^2}}$ (the **Bohr formula**). E_n are **energy states** or **levels** of the atom. E_0 is the **ground state**. The allowed electron radii are $r_n = \frac{\varepsilon_0 h^2}{\pi m_e e^2} n^2 = a_H n^2$, where $\boxed{a_H = 0.53\ \text{Å}}$ is the **Bohr radius**. The Bohr theory provides an explanation of the spectral emission from a hydrogen atom but does not describe the structure of atoms in which multiple electrons surround the nucleus.

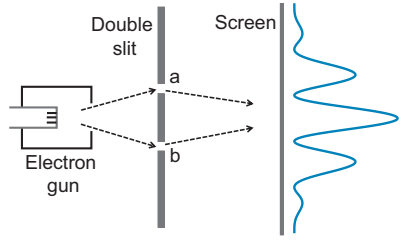
Wave–Particle Duality

In 1924, Louis de Broglie postulated that, like electromagmetic (EM) radiation, matter exhibits a dual nature, and its particles (such as electrons) should have wave properties. These waves are called **matter waves**.

Louis de Broglie introduced the relation for the electron wave $\boxed{\lambda_e = h/p_e}$, where $p_e = m_e v_e$ is the electron momentum in classical physics. Using the relation for the electron wavelength λ_e and Bohr's model for an atom, de Broglie obtained the condition for the angular momentum of the electron orbiting the nucleus. He assumed that an integer number n of electron wavelengths λ_e must fit into the circular orbit of the electron rotating around the nucleus, i.e., $2\pi r_n = n\lambda_e$. de Broglie obtained the condition for quantization of the electron angular momentum as

$$p_e r_n = m_e v_e r_n = n\hbar$$

where $\hbar = h/2\pi$ is the **reduced Planck constant**. Matter waves for electrons in atoms are standing waves corresponding to particular electron orbits.



A double-slit experiment, where electrons incident on the slits illuminate a screen placed beyond the slits, verified de Broglie's hypothesis. The amplitude of a matter wave represents the *probability* of finding the particle at a particular position. This probability imposes an inherent limitation on our knowledge of the particle's momentum and position.

The **Heisenberg uncertainty principle**, introduced by Werner Heisenberg in 1927, states that a certain pair of particle properties cannot be determined simultaneously. For example, the uncertainty in the measurement of position Δx and the uncertainty in the measurement of momentum Δp must satisfy the following inequality:

$$\boxed{\Delta p \Delta x \geq \hbar/2}$$

Wavefunction

When developing the theory of wave–particle duality, de Broglie introduced the plane wave (the **de Broglie wave**) $\Psi = \Psi_0 \exp[i(\vec{k}\,\vec{r} - \omega t)]$, which corresponds to a *free particle* with energy E and momentum $\vec{p}$. Here $\vec{k} = \vec{p}/\hbar$ is the wave vector, and $\omega = E/\hbar$ is the angular frequency. This idea stimulated the development of a new approach to describing the microworld. In 1926 and 1927, Schrödinger and Heisenberg independently developed two completely different techniques that provide probability descriptions of different parameters such as position and momentum instead of precise values of these parameters. These theories are known as **Schrödinger's wave mechanics** and **Heisenberg's matrix mechanics**. The two techniques are equivalent.

In wave mechanics, a **wavefunction** $\Psi(\vec{r}, t)$ is a mathematical expression involving the coordinate of a particle in space $\vec{r}$ and time t. In contrast to the de Broglie wave, a wavefunction describes not only a free particle, but also the particle in a force field. The wavefunction has no physical meaning, in itself, but the square of its absolute value

$$|\Psi|^2 = \Psi^* \Psi$$

is the **probability distribution function**. For example, $|\Psi|^2 dV$ is the probability that an electron is located within a volume dV. The total probability that the electron is located somewhere in space is presented by the relation

$$\int |\Psi|^2 dV = 1$$

Functions satisfying this equation are called **normalized functions**.

If Ψ_1 and Ψ_2 are wavefunctions, then any linear combination

$$a\Psi_1 + b\Psi_2$$

where a and b are arbitrary constants, is also a wavefunction. This is the hypothesis of **linear superposition**.

The Schrödinger Equation

The Schrödinger equation lies at the heart of wave mechanics. It cannot be derived; it must be postulated. When postulating Schrödinger's equation, one must keep in mind that it must be a linear equation in order to satisfy the hypothesis of linear superposition. The de Broglie wave must be its solution for a free particle.

Differentiating the de Broglie wave $\Psi = \Psi_0 \exp[i(\vec{k}\,\vec{r} - \omega t)]$ twice with respect to coordinates $\vec{r}$ and once with respect to time t results in two equations. Combining these two equations and considering that $\vec{k} = \vec{p}/\hbar$ and $\omega = E/\hbar$, one has the **Schrödinger equation for a free particle** (in the absence of force fields):

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi$$

where m is the mass of the particle.

In 1926, Erwin Schrödinger postulated his famous equation for a particle placed in a force field with uniform potential $V(\vec{r}, t)$:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(\vec{r}, t)\Psi$$

This equation is known as the **time-dependent Schrödinger equation**, which can be presented in operator form as

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

where $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$ is known as the **Hamiltonian operator** of the system, or the **energy operator**.

If neither the potential $V(\vec{r})$ nor any part of the system changes in time, the system can be described by the **time-independent Schrödinger equation**:

$$\hat{H}\Psi = E\Psi$$

where E is the energy of the system.

A Solution to the Schrödinger Equation

Let us consider a system with a potential $V(\vec{r})$ that does not change over time. We present the wavefunction of this system in the form

$$\Psi(\vec{r},t) = A(t)\varphi(\vec{r})$$

Substituting this wavefunction into the time-dependent Schrödinger equation, one obtains an equation that includes both the time-dependent $A(t)$ and the time-independent $\varphi(\vec{r})$ factors of the wavefunction:

$$A(t)\left[-\frac{\hbar^2}{2\,m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = i\hbar\frac{\partial A(t)}{\partial t}\varphi(\vec{r})$$

The time-independent factor of the wavefunction $\varphi(\vec{r})$ must be a solution to the time-independent Schrödinger equation,

$$\left[-\frac{\hbar^2}{2\,m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = E\varphi(\vec{r})$$

The solutions of the Schrödinger equation must be quadratically integrable. This requirement can only be satisfied for certain values of energy E, known as **eigenvalues** E_n. E_n are the characteristic energy levels of the system. The corresponding solutions $\varphi_n(\vec{r})$ are known as **eigenfunctions**.

The time-dependent factor of the wavefunction must satisfy the equation

$$A(t)E = i\hbar\frac{\partial A(t)}{\partial t}$$

The solution to this equation is written as

$$A(t) = A_0\exp(-iEt/\hbar)$$

where A_0 is a constant.

In this way, the wavefunction of the system has the form

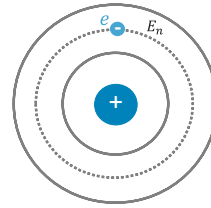
$$\boxed{\Psi_n(\vec{r},t) = \exp(-iE_nt/\hbar)\varphi_n(\vec{r})}$$

Quantum States

If an electron orbiting the nucleus has energy E_n, its probability distribution function

$$\begin{aligned}\Psi_n^*(\vec{r},t)\Psi_n(\vec{r},t) &= \varphi_n^*(\vec{r})\exp(iEt/\hbar)\varphi_n(\vec{r})\exp(-iEt/\hbar)\\ &= \varphi_n^*(\vec{r})\varphi_n(\vec{r})\end{aligned}$$

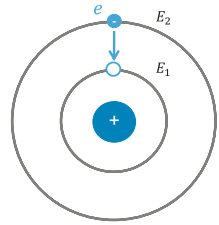
is constant in time, or *stationary*.



These states are called **stationary states**. The electron density of the atom in a stationary state is constant over time. The electromagnetic field is static. The atom *does not radiate*.

If an electron changes its state, its wavefunction must be a linear combination of its initial state with energy E_2 and its final state with energy E_1:

$$\begin{aligned}\Psi(x,y,z,t) &= C_1(t)\varphi_1(\vec{r})e^{-iE_1t/\hbar}\\ &\quad + C_2(t)\varphi_2(\vec{r})e^{-iE_2t/\hbar}\end{aligned}$$



where $C_1(t)$ and $C_2(t)$ vary with time slowly in comparison to the time-dependent exponential factors. In this case, the probability distribution function is written as

$$\begin{aligned}\Psi^*\Psi &= |C_1|^2|\varphi_1|^2 + |C_2|^2|\varphi_2|^2 + C_1^*C_2\varphi_1^*\varphi_2 e^{-i(E_2-E_1)t/\hbar}\\ &\quad + C_2^*C_1\varphi_2^*\varphi_1 e^{i(E_2-E_1)t/\hbar}\end{aligned}$$

The probability distribution is coherent and oscillating. This electron is in a **coherent state**. The oscillation between two energy states occurs at a frequency $\omega_{21} = (E_2 - E_1)/\hbar$, according to the second Bohr condition. Like an electric dipole, this electron is a source of *radiation*.

> In contrast to the electron energy in a stationary state, the energy of the electron in a coherent state is not well defined.

Quantum Mechanical Measurements

Unlike classical theory, quantum theory can predict only the probable results and not the exact results of a measurement. These probabilities can be determined with a **wavefunction** $\Psi(\vec{r},t)=\varphi(\vec{r})e^{-iEt/\hbar}$.

All acts of **quantum mechanical measurements** include an interaction between the particle and the observing apparatus. Each of these interactions has an **interaction duration time** Δt. The interaction with the apparatus can change the wavefunction of the particle. Let us consider an electron in the two-slit experiment (see page 17).

Before the measurement process occurs, the wavefunction of the electron is $\Psi=\Psi_a+\Psi_b$. The probability of finding the electron near the point with the position vector $\vec{r}$ is

$$P_{in}=|\Psi_a+\Psi_b|^2=|\varphi_a(\vec{r})|^2+|\varphi_b(\vec{r})|^2+\Psi_a^*\Psi_b+\Psi_a\Psi_b^*$$

where $\Psi_a^*\Psi_b$ and $\Psi_a\Psi_b^*$ are **interference terms**, which are absent in the case of the experiment where classical particles pass through these two slits. The observing apparatus "multiplies" each part of the wavefunction, Ψ_a and Ψ_b, by a random phase factor, α_a and α_b, respectively. Indeed, during the interaction duration time Δt, the energy in the oscillating term of the wavefunction $e^{-iEt/\hbar}$ is indefinite by some amount ΔE corresponding to the uncertainty principle $\Delta E\Delta t\geq\hbar/2$.

After the measurement, the wavefunction will be written as $\Psi=\Psi_a e^{i\alpha_a}+\Psi_b e^{i\alpha_b}$. The probability distribution is

$$\begin{aligned}P_{out}&=|\Psi_a e^{i\alpha_a}+\Psi_b e^{i\alpha_b}|^2=\\&=|\varphi_a(\vec{r})|^2+|\varphi_b(\vec{r})|^2+\Psi_a^*\Psi_b e^{-i(\alpha_a-\alpha_b)}\\&\quad+\Psi_a\Psi_b^* e^{i(\alpha_a-\alpha_b)}\end{aligned}$$

The **phase** $(\alpha_a-\alpha_b)$ fluctuates in a random way from one experiment to another. Terms with $e^{i(\alpha_a-\alpha_b)}$ will average out to *zero*. The interference between Ψ_a and Ψ_b is destroyed, resulting in a **collapse of the wavefunction**.

Operators and Expectation Values

The Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V$ is an energy operator with eigenvalues E_n and eigenfunctions φ_n. An arbitrary wavefunction of a system can be expressed as $\varphi = \sum_n C_n \varphi_n$, where C_n is a complex number representing the probability amplitude.

Suppose that one wants to measure the energy of a system that has a wavefunction φ before the measurement. In this case, $|C_n|^2$ is the *probability* of finding the system with energy E_n and a wavefunction φ_n after the measurement. C_n can be calculated as $C_n = \int \varphi \varphi_n^* d\vec{r} = \sum_m C_m \int \varphi_m \varphi_n^* d\vec{r}$, where $\int \varphi_m \varphi_n^* d\vec{r} = \delta_{mn}$, and $\sum_n |C_n|^2 = 1$. Here, δ_{mn} is the **Kronecker symbol**. Measuring the energy of the system, one could repeat the experiment many times and get a statistical distribution of results. The average value of the energy E that one would measure would be $\langle E \rangle = \sum_n |C_n|^2 E_n = \int \varphi^* \hat{H} \varphi d\vec{r}$. This average value is known as the **expectation value** of energy E.

In quantum mechanics, the expectation value $\langle f \rangle$ of any physically observable quantity f with the associated operator $\hat{f}$ is

$$\boxed{\langle f \rangle = \int \varphi^* \hat{f} \varphi d\vec{r}}$$

The **position operator** is trivial. This operator is the position vector $\vec{r}$, itself. It has a continuous set of eigenvalues.

The **momentum operator** is $\hat{p} = -i\hbar\nabla$, where ∇ is the **nabla operator**. This operator has eigenvalues $\hbar\vec{k}$, which are vectors.

The **angular momentum operator** is $\hat{L} = \hat{r} \times \hat{p} = -i\hbar(\vec{r} \times \nabla)$. This operator's z component in the spherical polar coordinates is $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$. It has eigenvalues $m\hbar$, where m is an integer.

The L^2 **operator** has the form $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\nabla_{\theta,\phi}^2$.

Its eigenvalues are $\hbar^2 l(l+1)$, where $l = 0, 1, 2, \ldots$.

Density Matrix

In quantum mechanics, the **Dirac bra-ket notation** can be used to present a quantum mechanical state (a **pure state**) of a system described with the wavefunction $\psi(\vec{r})$ as $|\psi(\vec{r})\rangle$. Each pure state can be expanded in terms of some complete orthogonal basis set as $|\psi(\vec{r})\rangle = \sum_n c_n|\varphi_n(\vec{r})\rangle$, where $|\varphi_n(\vec{r})\rangle$ are its basis states.

A pure state is an idealization. In Nature, statistical mixtures often take place. Each of these mixtures consists of subsystems (its members). A fraction of its members (with a relative population P_1) is in a pure state $|\psi_1\rangle$, some other fraction of its members (with a relative population P_2) is in a pure state $|\psi_2\rangle$, and so on. A system in a **mixed state** can be described with the **density matrix** introduced by John von Neumann and Lev Landau in 1927:

$$\rho = \sum_i P_i|\psi_i\rangle\langle\psi_i|$$

A mixed state is not a quantum superposition of pure states. The probabilities P_i in a mixed state are the probabilities of classical statistic theory. They are not the probability amplitudes in a quantum superposition. There is just one density matrix for each mixed state, whereas there are many statistical ensembles of pure states for each mixed state.

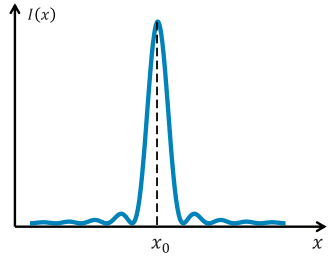
Unpolarized light is an example of a mixed state. It cannot be described with a pure state, but it can be considered as a statistical ensemble of pure states (left- and right-circularly polarized photons or vertically and horizontally linearly polarized photons).

Because for each of the pure states, $|\psi_i\rangle = \sum_i c_m^{(i)}|\varphi_i\rangle$, the density matrix is $\rho = \sum_{m,n}[\sum_i P_i c_m^{(i)}(c_n^{(i)})^*]|\varphi_m\rangle\langle\varphi_n|$, where * denotes the complex conjugate of a complex number. The matrix elements are $\rho_{mn} = \langle\varphi_m|\rho|\varphi_n\rangle = \overline{c_m c_n^*}$. The diagonal elements give the probabilities $|c_n|^2$ of finding the system in a specific state of the basis states $|\varphi_n\rangle$. The sum of the diagonal elements is unity: $Tr(\rho) = \sum_j \rho_{jj} = \sum_k P_k = 1$. Here, Tr stands for trace.

A state ρ is pure *if and only if* $\rho^2 = \rho$.

Wave Packet

According to the de Broglie hypothesis, a particle in free space with energy $E = \hbar\omega$ and momentum $\vec{p} = \hbar\vec{k}$ can be described by a traveling wave, which is a periodical function of $(\vec{k} \cdot \vec{r} - \omega t)$. This wave is spread over all space.



If a particle is restricted to a definite region of space, it must be described by a **wave packet**, which is a group of waves of slightly different wavelengths, with phases and amplitudes chosen such that they interfere constructively over only a small region of space. Outside of this region, these waves produce destructive interference with an amplitude that rapidly reduces to zero. The wave packet can be constructed by integrating plane waves over a small range of wavelengths. For example, in the case of light,

$$E(x) = \int_{k_0-\Delta k}^{k_0+\Delta k} e^{ik(x-x_0)}\,dk = 2\frac{\sin[\Delta k(x-x_0)]}{(x-x_0)}\,e^{ik(x-x_0)}$$

where $E(x)$ is the magnitude of the electric field in the complex representation. The intensity is

$$I(x) \sim |E(x)|^2 \sim \frac{\sin^2[\Delta k(x-x_0)]}{(x-x_0)^2}$$

The destructive interference begins to be important when $|x - x_0| > 1/\Delta k$, i.e., when

$$\boxed{\Delta x \Delta k \cong 1}$$

Here, Δx is the width of the wave packet in x space, and Δk is the width of the wave packet in k space. The wave energy is no longer uniformly distributed throughout the space. It is localized within the Δx area. Similar results can be obtained for the time interval Δt and the angular frequency range $\Delta\omega$ needed to form such a wave packet:

$$\boxed{\Delta\omega \Delta t \cong 1}$$

The Schrödinger Equation for Single-Electron Atoms

Here we apply a quantum mechanical treatment to a single-electron atom with a nuclear charge of $-Ze$. In this case, the time-independent Schrödinger equation in spherical polar coordinates is written as

$$-\frac{\hbar^2}{2m_r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] +V(r)\psi=E\psi$$

where $V(r)=-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$ is the Coulomb potential energy, $m_r=m_eM/(m_e+M)$, M is the nuclear mass, and ψ is a function of r, θ, and ϕ, and can be presented as $\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$. In this case, the Schrödinger equation can be written as

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)=-\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) -\frac{2m_r r^2\sin^2\theta}{\hbar^2}(E-V)$$

We set the first term on the left equal to $-m_l^2$. Dividing both sides of the equation by $-\sin^2(\theta)$ and equating them to $l(l+1)$, one obtains system of the equations:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m_r}{\hbar^2}(E-V)R=l(l+1)\frac{R}{r^2}$$

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_l^2\Theta}{\sin^2\theta}=l(l+1)\Theta$$

$$\frac{d^2\Phi}{d\phi^2}=-m_l^2\Phi$$

Solutions to these equations can be presented as

$$\Phi=\Phi_{m_l}(\phi)=e^{im_l\Phi}$$

$$\Theta=\Theta_{l,m_l}(\theta)=P_l^m(\cos\theta)$$

$$R(r)=R_{n,l}(r)=\rho^l e^{-\rho/2}L_{n+l}^{2l+1}(\rho),\ \text{where}\ \rho=2r/(na_H)$$

Quantum Numbers

To be physically meaningful, all solutions of the Schrödinger equation for single-electron atoms, $\psi(r,\theta,\phi) = \psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$, must be both single valued and finite everywhere.

This means that m_l in $\Phi_{m_l}(\phi) = e^{im_l\phi}$ must be an integer: $m_l = 0, \pm1, \pm2, \ldots$.

The solutions $\Theta_{l,m_l}(\theta) = P_l^m(\cos\theta)$ involve **Legendre polynomials**. They are finite only if l is an integer with values $|m_l|, |m_l|+1, |m_l|+2, \ldots$; i.e., $l \geq |m_l|$. For a given value of l, the integer m_l can take the values $-l, \ldots, -1, 0, +1, \ldots, +l$; i.e., $(2L+1)$ values of m_l are possible for each value l.

The solutions, $R_{n,l}(r) = \rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho)$, involve **associated Laguerre polynomials**. Here, the value $n = 1, 2, 3, \ldots$ is an integer, and it can only have values $n \geq l+1$.

The integers n, l, m are known as **quantum numbers**, as described below:

$n = 1, 2, 3, \ldots$, where $n \geq l+1$ is the **principal quantum number**. It specifies the **energy** of the electron in the atom.

$l = 0, 1, 2, \ldots (n-1)$ is the **orbital quantum number**. It specifies the **orbital angular momentum** of the electron in the atom.

$m_l = 0, \pm1, \pm2, \ldots, \pm l$ is the **magnetic quantum number**. It specifies the **orientation of the orbital angular momentum** of the electron in an external magnetic field.

Spectroscopy states with $l = 0, 1, 2, 3, \ldots$ are labeled as $s, p, d,$ and f, respectively. This means that the state $(n, l) = (3, 1)$ is labeled as $3p$.

The probability of finding an electron within a volume dV at (r, θ, ϕ) is

$$P_{n,l,m}(r,\theta,\phi)dV = [R_{n,l}^*(r)R_{n,l}(r)][\Theta_{l,m_l}^*(\theta)\Theta_{l,m_l}(\theta)][\Phi_{m_l}^*(\phi)\Phi_{m_l}(\phi)]dV$$

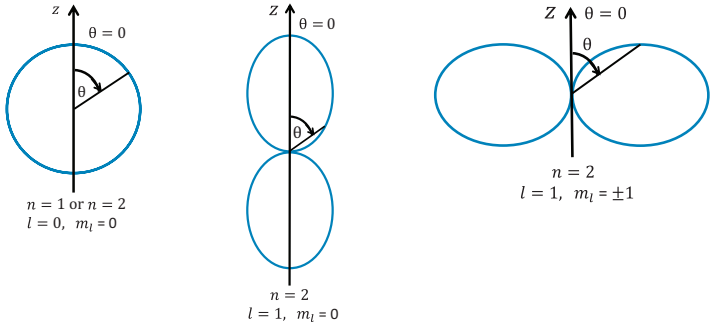
Selection Rules

The eigenfunction of the time-independent Schrödinger equation for a single-electron atom is

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$$

The radial dependence $R_{n,l}(r)$ contains an exponential term, meaning that the probability of finding the electron at $r \gg na_H$ is small.

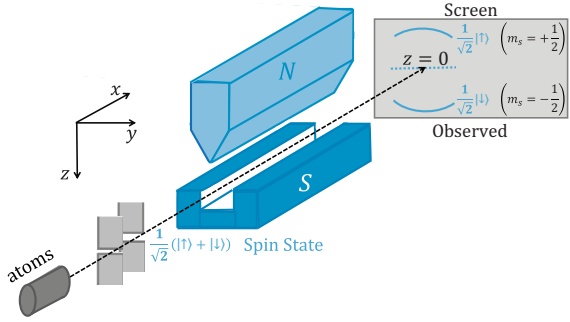
The probability $\Phi_{m_l}(\phi)\Phi^*_{m_l}(\phi) = 1$ for all single-electron eigenfunctions; i.e., the angular single-electron probability function does not depend on ϕ. It only depends on θ as $\Theta^*_{l,m_l}(\theta)\Theta_{l,m_l}(\theta)$. When $l \neq 0$, the probability of finding an electron is zero for certain directions relative to the z axis. This phenomenon is known as **space quantization**.



An atom that undergoes a transition can be considered as a charge cloud oscillating between the initial and the final distribution states. Like an oscillating electric dipole, it produces electromagnetic radiation with a rate determined by the electric dipole integral $\int \psi_f^*(r,\theta,\phi)\psi_i(r,\theta,\phi)dV$, which depends on the symmetry between the final ψ_f and the initial ψ_i eigenfunctions. This symmetry is determined by the quantum number l. The **electric dipole transition** (not **electric quadrupole** and **electric octupole transitions**) is possible only when

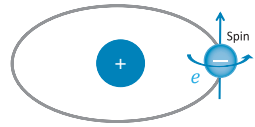
$$\boxed{\Delta l = \pm 1}$$ (a **selection rule**).

Electron Spin



In 1921, Otto Stern and Walther Gerlach tried to separate the various m_l components in a beam of atoms (in the **Stern–Gerlach experiment**). A beam of atoms is passed through a set of collimating slits. The beam then enters a region where an inhomogeneous magnetic field is normal to the direction of the motion of the atoms. In this inhomogeneous magnetic field, the atoms experience a force $\vec{F} = \nabla(\vec{m} \cdot \vec{H})$, where $\vec{m}$ is the magnetic moment of the atom, and $\vec{H}$ is the magnetic field. Since, in general, $\frac{\partial H_z}{\partial y}$ is small, we obtain $F_z \cong -\frac{e}{2m_e}\frac{\partial H_z}{\partial z}L_z$; i.e., F_z is proportional L_z. Atoms must be deflected according to their L_z values. $L_z = m_l\hbar$ due to space quantization. For example, for hydrogen atoms, with $l = m_l = 0$, only one undeflected beam is expected. However, the Stern–Gerlach experiment produces two quantized deflections. The surprising thing is that an *even* number of components is observed. Indeed, the number of m_l values $(2l + 1)$ is always *odd*.

In 1925, George Uhlenbeck and Samuel Goudsmit postulated that there is an *intrinsic* magnetic dipole moment of the electron $\vec{m}_S$, which is associated with an *intrinsic* angular momentum $\vec{S}$ (the **electron spin**) of the electron as $\vec{m}_S = -\frac{e}{m_e}\vec{S}$.



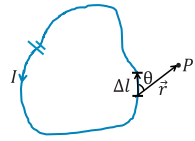
$$|\vec{S}|^2 = s(s+1)\hbar^2 \text{ and } S_z = m_s\hbar$$

where s is the **spin quantum number**, S_z is the component of $\vec{S}$ along the z axis, and m_s is the **spin magnetic quantum number**, which can take integers between $-s$ and s. For the electron, $|\vec{S}|^2 = \frac{3}{4}\hbar^2$, and $m_s = \pm\frac{1}{2}$.

Spin–Orbit Interaction

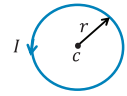
The **Biot–Savart law** permits one to calculate the magnetic field strength $\vec{H}$ at any point P in space created by a current I circulating in a circuit of arbitrary geometrical shape using the relation

$$\vec{H} = \frac{I}{4\pi}\oint \frac{d\vec{l}\times\vec{r}}{r^2}$$



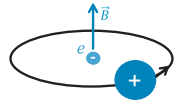
The magnitude of the magnetic field strength at the center of a circular coil with a current I is

$$|\vec{H}_c| = \frac{I}{4\pi R^2}\oint dl = \frac{I}{4\pi R^2}2\pi R = \frac{I}{2R}$$



In the Bohr model, an orbiting electron produces a current loop. The average current due to the orbiting electron is $I = -\frac{e}{T}$, where $T = \frac{2\pi r_n}{v}$ is the period of the rotation. Here, r_n is the radius and v is the frequency. This electron current can be presented as $I = -\frac{ev}{2\pi r_n} = -\frac{e}{2\pi m_e r_n^2}|\vec{L}|$, where $\vec{L}$ is the orbital angular momentum of the electron. Following the Biot–Savart law, the orbiting electron produces an **internal magnetic field** of the atom. In the area of the nucleus, this field is given as

$$|\vec{H}_n| = -\frac{e}{4\pi m_e r_n^3}|\vec{L}|$$



In the coordinate system associated with the electron, the nucleus is orbiting around the electron. In the case of a hydrogen atom, the nucleus charge equals the electron charge and has the opposite sign. Thus, the intrinsic spin magnetic dipole of the electron $\vec{m}_S$ experiences the internal magnetic field $\vec{H}$, which is similar to $\vec{H}_n$.

The potential energy of the spin magnetic dipole of the electron is $U = -\vec{m}_S \cdot \vec{B}$, where $\vec{B} = \mu_0\vec{H}$. Since $\vec{m}_S \propto \vec{S}$ and $\vec{B} \propto -\vec{L}$, the potential energy $U \propto \vec{S}\cdot\vec{L}$; i.e., U is proportional to the scalar product of the electron spin and the electron orbital angular momentum (the **spin–orbit interaction**). Because $m_s = \pm 1/2$, there are two possible directions for $\vec{m}_S$. As a result, all levels with $l \neq 0$ are split in two sublevels (the **fine structure**).

Total Angular Momentum of Single-Electron Atoms

The **total angular momentum** is the vector sum of the orbital angular momentum and the spin angular momentum.

For *single-electron atoms*, the total angular momentum is

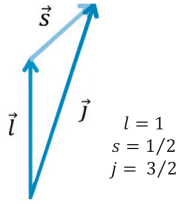
$$\vec{j} = \vec{l} + \vec{s}$$

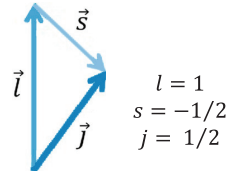
Its magnitude equals

$$|\vec{j}|^2 = j(j+1)\hbar^2$$

where j is the **total quantum number**:

$$j = l + s = l + \frac{1}{2} \quad \text{or} \quad j = l - s = l - \frac{1}{2} (l \neq 0)$$





Four quantum numbers, $n, l, s,$ and j, can be used to describe the energy levels. Each energy level with the quantum number n has sublevels, which are defined by the quantum numbers $l, s,$ and j. The number of such sublevels, $g = 2j + 1$, is called the **degeneracy** of the energy level. The spectroscopic-level notation is

$$n^{2s+1}l_j$$

Since for all single-electron atoms $2s + 1 = 2$, the notation nl_j can be used.

The orbital angular momentum quantum numbers l can be marked by letters as follows:

$$l = 0(s), 1(p), 2(d), 3(f), 4(g), 5(h), 6(i), 7(k), \ldots$$

As an example, $3s_{1/2}$ means $n = 3$, $l = 0$, and $j = 1/2$. In the case of $4d_{3/2}$, $n = 4$, $l = 2$, and $j = 3/2$.

Total Angular Momentum of Multi-Electron Atoms

For *multi-electron atoms*, two limiting coupling schemes take place: L–S coupling and *j*–*j* coupling.

If the electrostatic interaction between electrons dominates the spin–orbit interaction, **Russell–Saunders** (or **LS**) **coupling** takes place (introduced by Henry Russell and Frederick Saunders in 1925). The total spin and orbital angular momenta of the electrons are the vector sums

$$\vec{S} = \vec{s}_1 + \vec{s}_2 + \ldots + \vec{s}_N \text{ and } \vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots + \vec{l}_N$$

respectively. N is the number of **valence electron** in the atom. The total angular momentum of these electrons is the vector sum

$$\vec{J} = \vec{L} + \vec{S}$$

The spectroscopic-level notation has the form

$$^{2S+1}L_J$$

where S is the **total spin quantum number**, L is the **total orbital angular momentum quantum number**, and J is the **total angular momentum quantum number** of the level. L can be marked with letters according to

$$L = 0\,(S), 1\,(P), 2\,(D), 3\,(F), 4\,(G), 5\,(H), 6\,(I), 7\,(K), \ldots$$

The multi-electron energy levels split into sublevels as a result of electron–electron and electron–nucleus interactions. The number of these sublevels is known as the **multiplicity** of the level. The multiplicity equals $(2S+1)$ if $(2S+2) < (2L+1)$, or equals $(2L+1)$ if $(2L+2) < (2S+1)$.

For some heavier atoms, the spin–orbit interaction dominates the electrostatic interaction between electrons. These cases are referred to as ***j*–*j* coupling**. The total angular momentum of each electron in such atoms is

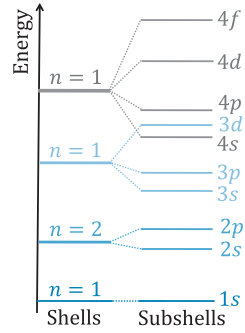
$$\vec{j}_k = \vec{l}_k + \vec{s}_k, \text{ and } \vec{J} = \sum_k \vec{j}_k$$

is the total angular momentum of the electrons.

Independent-Particle Approximation

The electron–electron interaction in multi-electron atoms leads to an extremely complicated **many-body problem**. A useful approximation is to assume that each electron moves independently of all other electrons in a spherically symmetric potential created by the Coulomb field of the nucleus and the other electrons (the **independent-particle approximation**). In this approximation, an electron state can be characterized in a similar way to the electron state of a single-electron atom, i.e., with four quantum numbers such as n, l, m_l, s; n, l, j, m_s; or n, l, m_l, m_s.

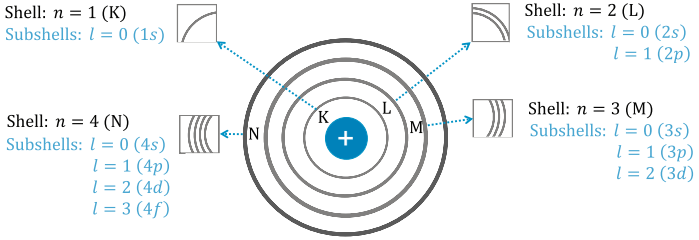
For each principal quantum number n, there are n possible values of the orbital quantum number l. For each l, there are $2l + 1$ possible values of the magnetic quantum number m_l. Each of these states has the spin magnetic quantum number $m_s = \pm 1/2$. Thus, there are $2\sum_{l=0}^{n-1}(2l + 1) = 2n^2$ states associated with each principal quantum number n.



Electrons with the same n belong to the same **shell**. Each shell can accommodate up to $2n^2$ electrons.

Electrons with the same n and l belong to the same **subshell** ($1s$, $2s$, $2p$, etc.). Each subshell can accommodate up to $2(2l + 1)$ electrons. The subshell filling order is $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $4f$, $5d$, $6p$, $7s$, $5f$, $6d$, ...

Unlike Bohr's theory, in the case of the independent-particle approximation, the energy depends on both n and l (but not on m_l or m_s).



Periodic Table of Elements

In 1869, Dmitri Mendeleev made a list of the then-known elements according to the observed periodicity in their physical and chemical properties. Today this list is known as the **periodic table of elements**.

Each atomic element can be described by the **atomic** or **proton number** Z, which equals the number of protons in its nucleus and its nucleus charge. The **neutron number** N equals the number of neutrons in the nucleus. The sum $A = Z + N$ is the **mass number** A.

The periodic table includes 18 vertical columns, with elements increasing in atomic number from left to right and from top to bottom. Elements in a given column (known as a **group**) have similar properties. The structure of the table can be understood using the concept of multi-electron atoms and the **Pauli exclusion principle** introduced by Pauli in 1925. According to this principle:

> No two fermions (including two electrons) can occupy the same quantum state; i.e., they cannot possess an identical set of quantum numbers.

The physical and chemical properties of the atomic elements are highly associated with their electron structures (known as **electron configurations**). For example, the electron configuration of the sodium (Na) atom is $1s^2 2s^2 2p^6 3s$. The Na atom has 11 electrons. The $1s$ and $2s$ subshells are occupied by two electrons each. The $2p$ subshell is occupied by six electrons. The $3s$ subshell is occupied by a single electron. Subshells, which are completely filled, are known as **closed subshells**. In the Na atom, $1s$, $2s$, and $2p$ are closed subshells.

The chemical reactivity of elements is linked to the number of electrons in an outer shell. Elements with a single electron in their outer shells (like sodium) are highly reactive. They form a column at left of the table. The "noble gasses" with full outer shells are unreactive. They form a column at the extreme right of the table.

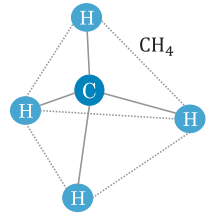
Mendeleev's Periodic Table

Classification of Simple Molecules

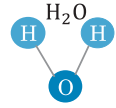
If atoms are located within distances on the order of the atomic dimensions, short-range forces bind these atoms together to make molecules. **Simple molecules** contain a few atoms joined by **covalent bonds**, which are based on the sharing of electron pairs between atoms. Simple molecules can be divided into four basic types, which include the following:

linear molecules

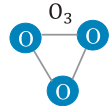
spherical-top molecules



asymmetrical-top molecules



symmetrical-top molecules



If a molecule contains N atoms, it has $3N$ degrees of freedom, including the three translational degrees of freedom, three rotational degrees of freedom about three axes, and a number value of $(3N - 6)$ vibrational degrees of freedom.

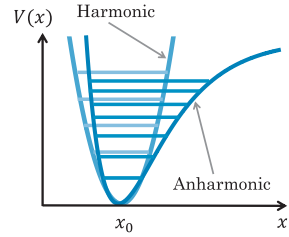
Linear molecules have two rotational degrees of freedom about three axes, and a number value of $(3N - 5)$ vibrational degrees of freedom. As with atoms, there are only certain allowed energy levels for the electrons of a molecule. However, unlike atoms, which have only electronic energy levels, molecules also have vibrational, rotational, and electronic levels.

Molecular Vibrations

Consider a diatomic molecule serving as a harmonic oscillator. The binding force that keeps the two atoms together is linear. The potential energy is $V(x) = \frac{1}{2}k_{sp}(x - x_0)^2$, where k_{sp} is the spring constant, x is the distance between the atoms, and x_0 is the distance in stable equilibrium. The vibrational motion is one-dimensional.

The total energy of the molecule is $E = \frac{1}{2}m_r\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}k_{sp}(x - x_0)^2$, where $m_r = \frac{m_1 m_2}{m_1 + m_2}$ is the **reduced mass**. In quantum mechanics, the allowed energies of the oscillator are quantized and equal $E_n = \hbar\omega(1/2 + n)$, where $n = 0, 1, 2, \ldots$, and $\omega = \sqrt{k_{sp}/m_r}$.

Real molecules are not harmonic oscillators. We can present their potential energy $V(x)$ as a Taylor series with $V(x_0) = 0$ and $(dV/dx_0)_{x=x_0} = 0$. $V(x)$ has a minimum at $x = x_0$. Thus, we have the anharmonic potential



$$V(x) = \frac{1}{2}k_{sp}(x - x_0)^2 + A(x - x_0)^3 + B(x - x_0)^4 + \ldots$$

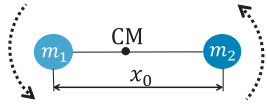
where A and B are constants. The **vibrational energies** are

$$E_v = hc\omega_e\left[\left(v + \frac{1}{2}\right) - x_e\left(v + \frac{1}{2}\right)^2 + y_e\left(v + \frac{1}{2}\right)^3 + \ldots\right]$$

where $v = 0, 1, 2, \ldots$ is the vibrational quantum number, $\nu_e = c\omega_e$ is the resonance frequency, and ω_e, x_e, y_e are tabulated values.

The selection rule for **vibrational transitions** within one vibrational mode in the harmonic system is $\Delta v = \pm 1$. In the anharmonic case, transitions with $\Delta v = \pm 2, \pm 3, \ldots$ are possible, but they are much weaker than the fundamental transitions with $\Delta v = \pm 1$.

Molecular Rotations

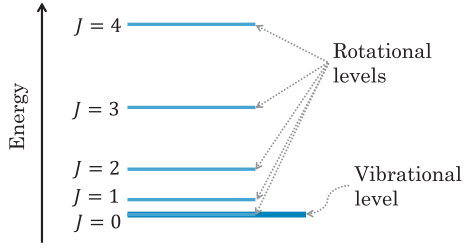


Consider a diatomic molecule, with masses m_1 and m_2, rotating about an axis through its center of mass (CM). Its moment of inertia is $I = m_r x_0^2$, where m_r is the reduced mass. The magnitude of the angular momentum vector is $L = I\omega_R$, where ω_R is the angular velocity of rotation. The kinetic energy of the molecule is $E = \frac{1}{2} I\omega_R^2 = \frac{L^2}{2I}$. The solution of the Schrödinger equation for the rotation of a rigid body gives the quantization of the angular momentum $L^2 = \hbar^2\, J(J+1)$, where $J = 0, 1, 3, \ldots$ is the angular momentum quantum number. Thus, the quantized rotational energy can be written as $E_J = hcBJ(J+1)$, where $B = \frac{h}{8\pi^2 cI}$. The molecule can vibrate, increasing the effective moment of inertia. This can be accounted for with $B = B_e - \alpha_e(v\frac{1}{2}+\ )$, where B_e and α_e are independent of the v and J tabulated constants. As the diatomic molecule rotates, the centrifugal force tends to increase both the distance between atoms and the moment of inertia I. Thus, the **rotational energy levels** associated with the vibrational level v can be written as

$$E_J = hc\left[B_e - \alpha_e\left(v + \frac{1}{2}\right)\right]J(J+1) - hcDJ^2(J+1)^2$$

In many applications, the **rigid-dumbbell approximation** can be used:

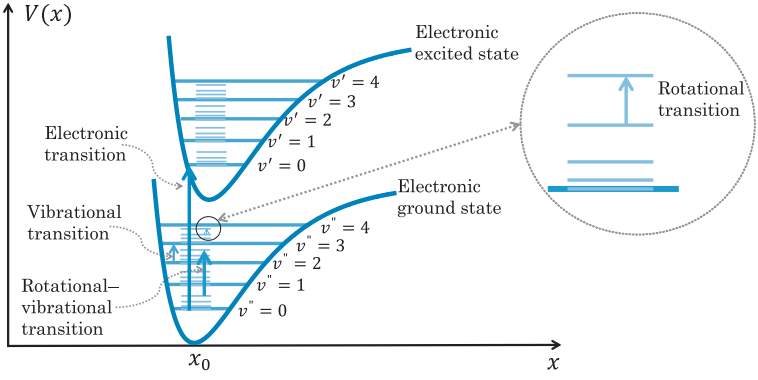
$$E_J \approx hcB_eJ(J+1)$$



The **selection rules** for rotational states are $\Delta J = 0, \pm 1$.

Molecular Transitions

The main ideas of the **Franck–Condon principle**, which is an important concept for analyzing **radiative transitions** in molecules, were proposed by James Franck in 1925. Franck's ideas were generalized by Edward Condon in 1926. Franck assumed that, when molecules absorb photons, the electron transitions from the ground state to excited states occur so rapidly that heavy nuclei do not have time to rearrange into their new equilibrium positions. Thus, in a diagram of molecular potential energy versus distance between nuclei, all upward or downward transitions must take place in a *vertical* direction.



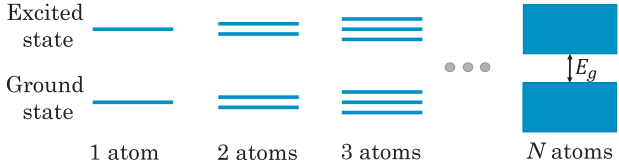
Electronic energy states have the largest energy separation. Transitions between electronic states (**electronic transitions**) typically produce emission in the visible or UV spectral regions.

Transitions between rotational states (**rotational transitions**) produce photons in the far-IR and microwave regions.

Rotational-level spacings are much smaller than vibrational-level spacing. Each vibrational level has a set of rotational sublevels. A radiative transition between rotational sublevels of the different vibrational levels is a **rotational–vibrational transition** and belongs to the mid-IR (MIR) region (37–100 THz or 3–8 μm).

Gases, Liquids, and Solids

In gases, the average distance between atoms or molecules is large compared to the particle dimensions. In liquids and solids, these values are comparable. The molecules in liquids and solids are strongly influenced by their neighbors. Consider two similar atoms having the exact same energy levels. If these atoms are brought close to each other, each of their levels turns into two sublevels with slightly different energies. The same process takes place in a system of three similar atoms. In this case, each level splits into three slightly separated sublevels.



When the number of atoms becomes comparable to the number of atoms in a macroscopic piece ($N \sim 10^{29}$ atoms/m^3), the N slightly separated sublevels of each atomic level form an **energy band**. The relatively large gaps between the bands become the **forbidden gaps**. The outer electrons of atoms are responsible for the energy bands' chemical and optical properties. In solids, the electrons in the highest energy bands—those bands that attain the highest occupied states of the individual atoms—are responsible for many important properties.

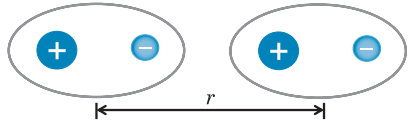
If the highest occupied energy band is only partially filled with electrons, the solid is a good **conductor** of electricity.

If the highest occupied energy band is completely filled with electrons, the solid is an electrical **insulator** because its electrons cannot flow freely when an electric field is applied. For insulators, the forbidden energy gap E_g is large compared to the energy that an electron picks up in the applied field. Basically, in insulators, $E_g > 4$ eV. Solids with $E_g < 4$ eV are referred to as **semiconductors**. For example, SiO_2 (9 eV) is an insulator; Ge (0.75 eV), Si (1.1 eV), and GaAs (1.42 eV) are semiconductors.

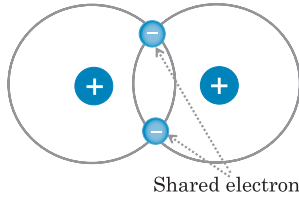
The van der Waals Interaction and Covalent Solids

The structure and properties of a solid are determined by the forces acting among the atoms that make up the solid. Here we consider the nature of these forces.

In some solids, the bonding is based on the very weak **van der Waals interaction**, which results from an induced electric dipole–dipole interaction. There is no charge transferred between atoms. The attractive van der Waals interaction depends on the interatomic separation to the inverse sixth power ($\sim r^{-6}$). This interaction is short-ranged, acting essentially only between nearest-neighbor pairs of atoms. The van der Waals interaction is responsible for formation of **rare-gas solids** and **molecular solids**, including many organic compounds, all of which are poor conductors. Due to the weakness of the van der Waals interaction, molecular solids are much easier to deform or compress than covalent or ionic solids.

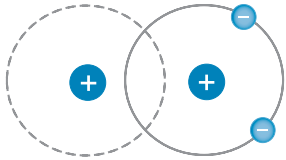


Covalent solids, which include diamond and silica (SiO_2), among other elements, are also known as **covalent-network solids** or **atomic solids**. These are solids with **covalent bonds**. The bonds are based on the overlap of partially occupied electron orbitals of two neighboring atoms, which leads to a lowering of the overall electronic energy. Since there are no mobile electrons in covalent solids, these solids are poor electrical conductors. Covalent bonds tend to hold the atoms tightly together and arranged in fixed geometries. They cause covalent solids to be hard and to have high melting points.

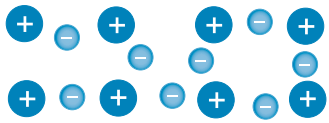


Ionic and Metallic Solids

In **ionic solids** such as NaCl, a complete charge transfer takes place between different atoms. The atoms become positively charged ions (**cations**), e.g., Na^+, and negatively charged ions (**anions**), e.g., Cl^-. The dominant attractive interaction between the ions is the Coulomb electrostatic interaction with an r^{-1} dependence characteristic. This ionic interaction is long ranged. The ionic force is not limited to the nearest neighbors but extends to very distant ions. The ionic interaction is also centrosymmetric, i.e., symmetric with respect to a central point. Structures with large numbers of conjugate ions around a given ion are low-energy structures. In ionic solids, electrons are tightly held by the ions, so there are no free electrons. As a result, ionic solids do not conduct electricity.



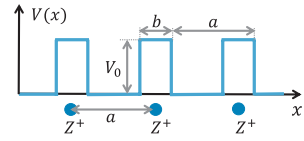
In a **metallic solid** such as copper, silver, or gold, the electrons are not all tightly bound. In metals, the atoms are ionized and form cations. The electrons form a delocalized **electron gas** within which the ion cores are dispersed. The ionization takes place because metals are formed from atoms in which the outer electrons are in unfilled configurations. The metallic interaction is nondirectional; i.e., in metallic solids, the ion packing density is maximized. Metallic solids are good conductors. The electrons of a metal can be considered as completely free to move. Of course, this is an approximation. Electrons are not completely free in metals. As soon as electrons move through the metal, they suffer collisions with other electrons and fixed cations. As a result, all metals have a finite resistance.

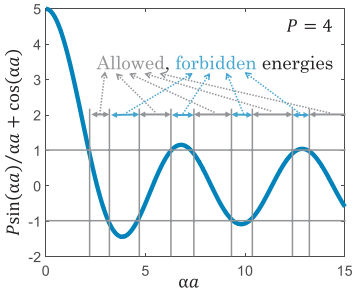


Energy Bands in Solids

Let us assume that all atoms in a crystal are fixed. Then the sum over the potentials of all atoms forms a periodic potential for the electrons. We will have a Hamiltonian for about 10^{29} interacting outer electrons per cubic meter (m^3). This approach can be simplified with a **single-electron approximation**. In this approximation, all atoms and all interaction potentials between electrons form a periodic potential $V(\vec{r}) = V(\vec{r} + \vec{R})$, where $\vec{R}$ is a translation vector of the lattice. One needs to calculate the eigenstates for *one* electron using the Schrödinger equation, which includes this potential. These eigenstates must be filled with available electrons according to Fermi–Dirac statistics.

For simplicity, consider a 1D solid, which can be described with the Schrödinger equation, $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0$, where $V(x+a) = V(x)$. According to **Bloch's theorem**, its solution must be of the form $\psi(x) = u(x)e^{ikx}$. Here, $u(x+a) = u(x)$. Different potentials $V(x)$ can be used to describe different 1D solids. The series of square wells proposed by Ralph Kronig and William Penney in 1930 is a particularly simple choice.





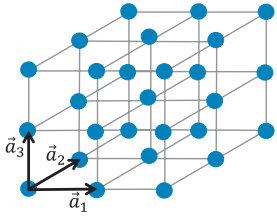
Solving the Schrödinger equation with the **Kronig–Penney potential energy model**, and accounting for the approximations $b \to 0, V_0 \to \infty, V_0 b = constant$, one can obtain the equation that connects the wave vector k and the energy E:

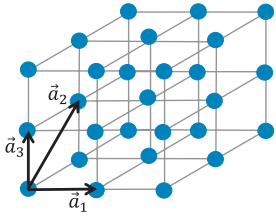
$$\cos(ka) = \cos(\alpha a) + P\frac{\sin(\alpha a)}{\alpha a}, \text{where } \alpha = \frac{\sqrt{2mE}}{\hbar}, P = \frac{mV_0 ba}{\hbar^2}$$

P describes the "strength" of the periodic potential. The values of α for which $|P\sin(\alpha a)/\alpha a + \cos(\alpha a)| > 1$ define the forbidden values of the energy E.

Crystal Lattice

A crystal lattice (also known as a lattice) can be presented as an infinite array of mathematical points in 3D space, having the translational periodicity characteristic of the crystal. A lattice is defined by the three **fundamental translation vectors** $\vec{a}_i$ $(i = 1, 2, 3)$. These vectors belong to the real lattice. This set is not unique. There are many ways of choosing the translational vectors for a given lattice.



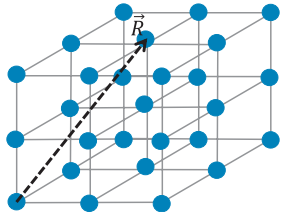


A geometric object with volume

$$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

is known as a **unit cell**. The whole volume of a crystal is completely filled with identical unit cells. The unit cell and the fundamental translation vectors $\vec{a}_i$ $(i = 1, 2, 3)$ forming this unit cell are called **primitive** if the unit cell has the minimum possible volume.

Crystals show long-range order. If we start with a specific atom, we will reach an identical atom if we shift by the vector $\vec{R}$, called a **translation vector** of the lattice.

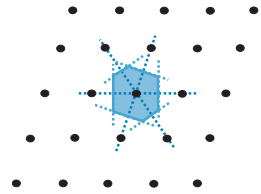


$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

where $n_i = 0, \pm 1, \pm 2, \ldots$

The infinite matrix of points generated by the vector $\vec{R}$ is known as a **Bravais lattice**, named after Auguste Bravais. There are 14 possible Bravais lattices in 3D space.

Reciprocal Lattice



The **Wigner–Seitz cell** can be obtained by connecting a lattice point to all other neighboring lattice points and drawing the lines (for a 2D crystal) or the planes (for a 3D crystal) perpendicular to these connecting lines and passing through their midpoints. The Wigner–Seitz cell is atom-centered. It is possible to fill the entire space by translation of that primitive unit cell.

Let us consider an arbitrary function $f(\vec{r})$ in the space of a lattice whose periodicity is given as $f(\vec{r}+\vec{R}) = f(\vec{r})$, where $\vec{R}$ is the real-space **translation vector**. The function $f(\vec{r})$ can be expanded in a Fourier series as

$$f(\vec{r}) = \sum_K f_K e^{i(\vec{K}\cdot\vec{r})}$$

where

$$f_K = \frac{1}{V_c}\int_{V_c} f(\vec{r}) e^{i(-\vec{K}\cdot\vec{r})} d\vec{r}$$

and $\vec{K}$ is a **general translation vector** of the **reciprocal lattice**. This vector can be presented as

$$\vec{K} = l_1\vec{b}_1 + l_2\vec{b}_2 + l_3\vec{b}_3$$

where $l_j = 0, \pm 1, \pm 2, \ldots$ and $j = 1, 2, 3$. The vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are **elementary translational vectors of the reciprocal lattice**:

$$\vec{b}_1 = \frac{2\pi}{V_c}\vec{a}_2 \times \vec{a}_3,\ \vec{b}_2 = \frac{2\pi}{V_c}\vec{a}_3 \times \vec{a}_1,\ \vec{b}_3 = \frac{2\pi}{V_c}\vec{a}_1 \times \vec{a}_2$$

$\vec{a}_{1,2,3}$ are fundamental translation vectors of a real lattice.

$$\vec{R}\cdot\vec{K} = 2\pi M, \text{ where } M = 0, \pm 1, \pm 2, \ldots$$

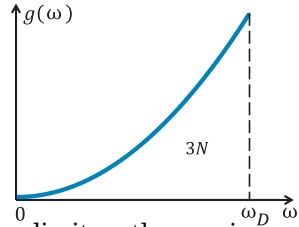
The Wigner–Seitz cell of a reciprocal lattice is called the **Brillouin zone** (introduced by Léon Brillouin in 1930).

The Debye Frequency

An acoustic (sound) wave is an elastic wave propagating in a medium. It can be described as $\vec{u}(\vec{k},t)=\vec{u}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$, where $\vec{u}$ is an instantaneous displacement, $\vec{u}_0$ is the polarization vector, and $\vec{k}$ is the wave vector. There are two independent **transverse acoustic** (TA) **modes** and a **longitudinal acoustic** (LA) **mode** propagating with velocities v_t and v_l, respectively. In the TA modes, vectors $\vec{u}_0$ are perpendicular to each other and both are perpendicular to vector $\vec{k}$. In the LA mode, $\vec{u}_0$ is parallel to $\vec{k}$. Consider a cube of side L. The allowed values of $\vec{k}$ can be obtained from the boundary condition, which states that an antinode of the amplitude should exist at each surface, or $k_i = n\frac{\pi}{L}$, where $i=x,y,z$, and $n=0,1,2,3,\ldots$. The volume of k-space corresponding to one k value is $V_k=(\pi/L)^3$. The k-space density of standing-wave states is $\rho_k = V/\pi^3$, where $V=L^3$. The number of allowed standing-wave states having wave vectors between k and $k+dk$ equals the volume of the positive octant of a spherical shell of radius k and thickness dk multiplied by the k-space density ρ_k:

$$g_i(k)dk=\frac{1}{8}\frac{V}{\pi^3}4\pi k^2dk=\frac{Vk^2dk}{2\pi^2}\Rightarrow g(\omega)d\omega=\frac{3V\omega^2d\omega}{2\pi^2v_0^3}$$

where $v_0=\sqrt[3]{3}(2v_t^{-3}+v_l^{-3})^{-1/3}$. $g(\omega)d\omega$ is the *total* vibrational density of states, i.e., the number of standing-wave states with frequencies between ω and $\omega+d\omega$, including the TA and LA modes. If the sample contains N atoms, the total $3N$ degrees of freedom imposes a limit on the *maximum* frequency ω_D that can exist in the system. One can calculate ω_D as



$$3N=\int_0^{\omega_D}g(\omega)d\omega=\frac{3}{2\pi^2}\frac{V}{v_0^3}\int_0^{\omega_D}\omega^2d\omega$$

from which we can obtain

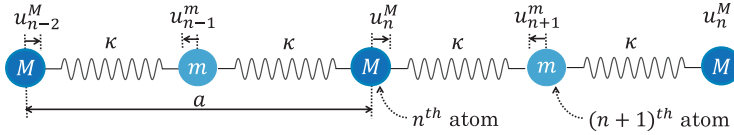
$$\omega_D=v_0\left(\frac{6\pi^2N}{V}\right)^{1/3}\text{(the Debye frequency)}.$$

Lattice Vibrations

Consider a periodic 1D chain consisting of two types of atoms with masses M and m ($M > m$), separated by a distance $a/2$ and connected by identical springs. Here, a is the unit-cell spacing. Two **equations of motion** can describe the vibrating M and m masses:

$$M\frac{\partial^2 u_n^M}{\partial t^2} = -\kappa(2u_n^M - u_{n+1}^m - u_{n-1}^m) \quad \text{for mass } M$$

$$m\frac{\partial^2 u_{n-1}^m}{\partial t^2} = -\kappa(2u_{n-1}^m - u_n^M - u_{n-2}^M) \quad \text{for mass } m$$



Here, u_n^M is the displacement of the n^{th} atom with the mass M. Let us assume that the displacements have the form

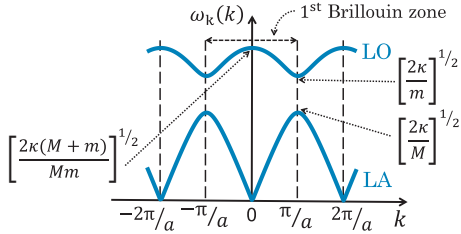
$$u_n^M = Ae^{-i(kx_n^0 - \omega_k t)} \text{ and } u_n^m = \alpha Ae^{-i(kx_n^0 - \omega_k t)}, \text{ where } x_n^0 = \frac{na}{2}$$

Substituting the relations u_n^M and u_n^m in the equations of motion, one can obtain the relation

$\alpha = \frac{2\kappa\cos(ka/2)}{2\kappa - \omega_k^2 m} = \frac{2\kappa - \omega_k^2 M}{2\kappa\cos(ka/2)}$, from which one can obtain

$$\omega_k^2(k) = \frac{\kappa(M+m)}{Mm} \pm \kappa\left[\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2(ka/2)\right]^{\frac{1}{2}}$$

As can be seen from this relation, for any value of k, there are two frequencies. These frequencies form the **dispersion curves**, which are periodical with a period of $2\pi/a$ in reciprocal space.



Lattice Vibrations (cont.)

Consider the dispersion branches near $k \ll 1/\alpha \approx 0$ (the long-wavelength limit) and $k \approx \pm\pi/\alpha$ (1st Brillouin zone boundary).

- If $k \ll 1/\alpha \approx 0$

  $\omega_k^2 \cong \dfrac{\kappa\alpha^2 k^2}{2(M+m)}$ with $\alpha = 1$ for the LA branch

  $\omega_k^2 \cong \dfrac{2\kappa(M+m)}{Mm}$ with $\alpha \cong 1 - M/m$ for the LO branch

- If $k \approx \pm\pi/\alpha$

  $\omega_k^2 = \dfrac{2\kappa}{M}$ with $\alpha = 0$ for the LA branch

  $\omega_k^2 = \dfrac{2\kappa}{m}$ with $\alpha = \infty$ for the LO branch

In the lower branch, the two types of atoms oscillate with the same phase and amplitude in what is known as the **longitudinal acoustic** (LA) **mode**.

In the upper branch, the two types of atoms oscillate in antiphase. Their centers of mass are at rest. This branch can be excited by the electric field of light in what is known as the **longitudinal optical** (LO) **mode**.

In the LA branch, masses m are at rest and masses M oscillate. In the LO branch, masses M are at rest, and masses m oscillate.

Contrary to the 1D model, in 3D solids, transverse modes are allowed. These modes include the **transverse acoustic** (TA) and **transverse optical** (TO) **modes**. In these modes, vibrations occur in the plane that is perpendicular to the direction of propagation.

If a crystal cell contains p atoms, there are $3p$ different branches of vibrational dispersion. These include *three* acoustic (one LA and two TA) modes, and the remaining $3(p-1)$ modes are optical modes, of which $(p-1)$ are LO modes and $2(p-1)$ are TO modes.

Quantized Vibrational Modes

In solids, **vibrational excitations** are the collective, independent normal modes with frequencies $\omega_k(\vec{k})$ that are functions of wave vector $\vec{k}$. In the quantum mechanical approach, each normal mode can be treated as an independent harmonic oscillator with frequency ω_k. The energy of this oscillator is quantized, meaning that it can only take the values

$$E_k^p = [1/2 + n_k^p]\hbar\omega_k, \text{ where } n_k^p = 0, 1, 2, \ldots$$

Here, $E_k^{p0} = \hbar\omega_k/2$ is the **zero-point energy**. The total vibrational energy is the sum of the energies of each of the normal modes $E = \sum_{k,p} E_k^p$. The quantized elastic waves can be considered as quasi-particles (**phonons**). By direct analogy with the case of a quantized EM field (Planck's law for cavity radiation)—where the allowed energies of a normal mode of the radiation field in a cavity are given by the relation $(1/2 + n)\hbar\omega$, where n is the number of photons with frequency ω—the value n_k^p can be treated as the number of phonons with wave vector $\vec{k}$ or frequency ω_k. The phonon's quasi-impulse is $\hbar\vec{k}$. The phonon's velocity is $v_{phon}(\vec{k}) = \partial\omega(\vec{k})/\partial\vec{k}$. The number of phonons n_k^p depends on the temperature T. This dependence can be calculated using methods of statistical mechanics. The partition function Z for phonons associated with the normal modes of a crystal can be defined as

$$Z = \sum_{i=1}^{\infty} e^{\left(-\frac{E_i}{\kappa_B T}\right)} = \sum_{n_k^p=0}^{\infty} e^{\left(-\frac{(1/2+n_k^p)\hbar\omega_k}{\kappa_B T}\right)} = \frac{e^{\left(-\frac{\hbar\omega_k}{2\kappa_B T}\right)}}{1 - e^{\left(-\frac{\hbar\omega_k}{\kappa_B T}\right)}}$$

From the mean energy $\langle E\rangle$, in thermal equilibrium, one can obtain the **mean phonon-occupation number** $\langle n_k^p(\omega_k, T)\rangle$ as

$$\langle E\rangle = \kappa_B T^2 \frac{\partial(\ln Z)}{\partial T} = \frac{1}{2}\hbar\omega_k + \frac{\hbar\omega_k}{e^{\left(\frac{\hbar\omega_k}{\kappa_B T}\right)} - 1}$$

$$\Rightarrow \boxed{\langle n_k^p(\omega_k, T)\rangle = \frac{1}{e^{\left(\frac{\hbar\omega_k}{\kappa_B T}\right)} - 1}}$$

Here, $\langle \ldots \rangle$ indicates a thermal average. This is the Planck distributions law, which is also valid for photons. Phonons are bosons. The number of phonons in a given state is unlimited.

Classification of Light–Matter Interaction Processes

Processes of light–matter interaction are divisible into parametric and nonparametric processes, as well as steady state and transient processes, depending on different parameters.

In **parametric processes**, the initial and final quantum-mechanical states of the system must be the same. In these processes, the population of the ground state can be excited to a virtual level and can reside in the virtual level for a short time interval. *Photon energy conservation* should always be met in a parametric process. Parametric processes can be described by a *real susceptibility*. Parametric processes include second-harmonic generation, sum- and difference-frequency generation, optical parametric oscillation, third-harmonic generation, and self-focusing, among others.

In **nonparametric processes**, an *energy exchange* with the material medium takes place. The population of the ground state must be transferred to an excited state. Nonparametric processes can be described by a *complex susceptibility*. Nonparametric processes include Raman and Brillouin scattering, among others.

> The real part of the refractive index corresponds to parametric processes. The imaginary part of the refractive index, which describes the radiation absorption, corresponds to nonparametric processes.

In **steady-state processes**, laser light is applied to a system during a time interval τ_L, which considerably exceeds the response time τ_{res} and the relaxation time τ_{rel} of the system; i.e., $\tau_L \gg \tau_{res},\ \tau_{rel}$.

If the time interval during which laser light is applied to the system satisfies the relation $\tau_L \ll \tau_{res},\ \tau_{rel}$, **transient processes** take place in the system.

Some non–steady-state effects, such as, e.g., superradiance, self-induced transparency, and photon echo, are not available in the case of steady-state light–matter interaction.

Rabi Frequency

The interaction of a bound electron with light can be described by the **time-dependent Schrödinger equation**,

$$i\hbar\frac{\partial\psi}{\partial t} = (H_0 + H_I)\psi$$

H_0 is the kinetic energy plus the potential energy of the electron associated with its binding to the nucleus. $H_I = -e\vec{x}\cdot\vec{E}$ is the electron–EM-field interaction energy. In a two-state system, the wavefunction for an atomic electron can be presented as $\psi(\vec{x},t) = a_1(t)\varphi_1(\vec{x}) + a_2(t)\varphi_2(\vec{x})$, where $\vec{x}$ is the electron–nucleus distance. We introduce $c_1(t) = a_1(t)$ and $c_2(t) = a_2(t)e^{-i\omega t}$, where ω is the field frequency. Substituting $\psi(\vec{x},t)$ in the time-dependent Schrödinger equation, and considering that

> the $e^{-i\omega t}$ terms for optical frequencies ω can be averaged to zero over a realistic time interval [the **rotating-wave approximation** (RWA)],

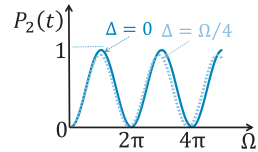
one can obtain the following relations:

$$c_1(t) = \left(\cos\frac{\Omega t}{2} + i\frac{\Delta}{\Omega}\sin\frac{\Omega t}{2}\right)e^{-i\Delta t/2}, c_2(t) = i\frac{\Omega_R}{\Omega}\sin\frac{\Omega t}{2}e^{-i\Delta t/2}$$

where $c_1(0) = 1$, $c_2(0) = 0$, and $\Omega = \sqrt{{\Omega_R}^2 + \Delta^2}$ is the **generalized Rabi frequency**. $\Delta = \omega_0 - \omega$ is the detuning, and $\Omega_R = (e\vec{x}_{21}\cdot\hat{\varepsilon})E_0\hbar^{-1}$ is the field–atom interaction energy in frequency units. It is called the **resonance Rabi frequency**. Here, $\vec{x}_{21} = \int\varphi_1^*(\vec{x})\vec{x}\varphi_2(\vec{x})d^3x$, E_0 is the amplitude of the applied electric field, and $\hat{\varepsilon}$ is the unit vector that defines the field polarization. The probabilities of finding the electron in the upper ($P_2(t) = |a_2(t)|^2$) state and lower ($P_1(t) = |a_1(t)|^2$) state are

$$P_1(t) = \frac{1}{2}\left[1 + \left(\frac{\Delta}{\Omega}\right)^2\right] + \frac{1}{2}\left(\frac{\Omega_R}{\Omega}\right)^2\cos\Omega t, P_2(t) = \frac{1}{2}\left(\frac{\Omega_R}{\Omega}\right)^2[1 - \cos\Omega t]$$

> The generalized Rabi frequency is the frequency at which the probability oscillates between levels 1 and 2.



The Stark Effect

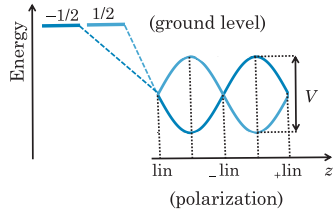
In 1913, Johannes Stark discovered that the spectral lines of atoms, ions, and molecules undergo splitting in an externally applied electric field (the **Stark effect**). If the charge distribution is microscopic, the applied macroscopic electric field can be considered as a uniform field over the charge distribution.

If an atom is placed in an external *static* electric field $\vec{E}$, its energy levels will shift by $\Delta E = \vec{p} \cdot \vec{E}$, where $\vec{p} = \alpha(\omega)\vec{E}$ is the atomic dipole moment, and $\alpha(\omega)$ is the complex polarizability. This effect is known as the **DC Stark effect**.

If an atom is placed in an *oscillating* electric field (e.g., that of a laser) the **AC Stark effect** (or the **Autler–Townes effect**) takes place. The average energy shift (light shift) is

$$\Delta E \approx -\frac{C^2}{2}\frac{|\Omega_R|^2}{\Delta}$$

where Ω_R is the Rabi frequency, $\Delta = \omega - \omega_0$ is the detuning, and C is the relevant **Clebsch–Gordon** (CG) **coefficient**.



Consider an atom that has orbital angular moment quantum numbers $J = 1/2$ and $J = 3/2$ for the ground and exited states, respectively. This means that the ground level has only two magnetic sublevels, $m = \pm 1/2$, and the excited level has four magnetic sublevels, $m = \pm 1/2, \pm 3/2$. We assume that the laser intensities are sufficiently small that excited-state populations are negligible. The intensity of $\sigma_\pm$ polarized light is $I(\sigma_\pm) = I_0(1 \mp \sin 2\,kz)/2$, where I_0 is the maximum intensity. The light shifts of the two ground sublevels, with $m = \pm 1/2$ due to the existence of these $\sigma_\pm$ polarization modes, are

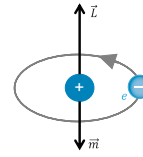
$$\Delta E_\pm = -\frac{\hbar \Delta \Omega_R^2}{\gamma_0^2 + 4\Delta^2}(2 \mp \sin 2\,kz)$$

where γ_0 is the atomic transition linewidth.

The Zeeman Effect

The splitting of atomic levels in the presence of a magnetic field (known as the **Zeeman effect**) was discovered in 1896 by Pieter Zeeman.

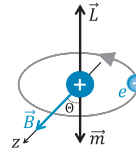
An orbiting electron in an atom forms a current loop with a magnetic dipole momentum $\vec{m}$, which is related to the orbital angular momentum $\vec{L}$ as



$$\vec{m} = -\frac{e}{2m_e}\vec{L}$$

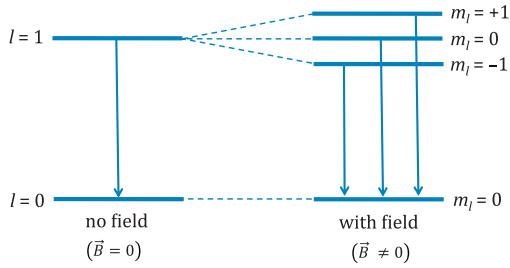
where m_e and e are electron mass and charge, respectively, and $|\vec{L}|^2 = l(2l+1)\hbar^2$. As a result of the space quantization of the angular moment, $\vec{L}$ is limited to certain directions with respect to the z axis. Its components along the z axis satisfy the equation $L_z = m_l\hbar$.

Now we apply a magnetic field $\vec{B}$ along the z axis. The potential orientational energy U associated with the orientation of $\vec{m}$ is



$$U = -\vec{m}\cdot\vec{B} = -|\vec{m}||\vec{B}|\cos\theta = m_l\mu_B|\vec{B}|$$

where $\mu_B = \frac{e\hbar}{2m_e}$ is the **Bohr magneton**. U is quantized with the quantum number m_l. Hence, m_l degeneracy is removed by the external magnetic field. There are $(2l+1)$ values of m_l for each l. The level splits into $(2l+1)$ components (the **normal Zeeman effect**). Not all level splitting can be explained by the normal Zeeman effect. Some splitting of the levels can be explained by the **anomalous Zeeman effect**, which accounts for the electron spin.



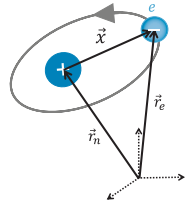
The Electron Oscillator Model

The **electron oscillator model** is part of classical theory, which treats the interaction of light with matter. It is based on a hypothesis introduced by Hendrik Lorentz around 1990, which states that an electron in an atom responds to the applied electromagnetic field as if it were bound to the nucleus with a spring. In classical physics, a charged particle in an electromagnetic field experiences the **Lorentz force** $\vec{F} = e(\vec{E} + \vec{v} \times \vec{B})$, where e is the charge of the particle, and $\vec{v}$ is its velocity.

Newton's laws of motion for the electron and nucleus are

$$m_e \frac{d^2}{dt^2}\vec{r}_e = e\vec{E}(\vec{r}_e, t) + \vec{F}_{en}(\vec{x})$$

$$m_n \frac{d^2}{dt^2}\vec{r}_n = e\vec{E}(\vec{r}_n, t) + \vec{F}_{ne}(\vec{x})$$



where $m_{e,n}$ are the electron (e) and nucleus (n) masses, respectively. $\vec{F}_{en}$ is a binding force that the nucleus exerts on the electron. It depends on their relative separation: $\vec{x} = \vec{r}_e - \vec{r}_n$. $\vec{F}_{ne}$ is the force that the electron exerts on the nucleus. $\vec{F}_{en} = -\vec{F}_{ne}$. The electric field is not sensitive to variations as small as an atomic dimension $|\vec{x}|$; i.e., $\vec{E}(\vec{r}_e, t) \cong \vec{E}(\vec{r}_n, t)$. Accounting for this approximation, we can write

$$m_r \frac{d^2}{dt^2}\vec{x} = e\vec{E}(\vec{R}, t) + \vec{F}_{en}(\vec{x})$$

where $\vec{R} = \frac{m_e\vec{r}_e + m_n\vec{r}_n}{(m_e + m_n)}$, and $m_r = \frac{m_e m_n}{(m_e + m_n)}$. According to the Lorentz assertion concerning a hypothetical elastic force, one can replace $\vec{F}_{en}(\vec{x})$ with $-k_{sp}\vec{x}$. In this case,

$$m_r \frac{d^2}{dt^2}\vec{x} = e\vec{E}(\vec{R}, t) - k_{sp}\vec{x} \quad \text{or} \quad \frac{d^2}{dt^2}\vec{x} + \omega_0^2\vec{x} = \frac{e}{m_r}\vec{E}(\vec{R}, t)$$

where $\omega_0^2 = k_{sp}/m_r$. The Lorentz model describes only how light interacts with an atom; it does describe not the atom itself.

Spontaneous Emission

In the absence of an eternal field $\vec{E}$, the electron oscillator equation is

$$\frac{d^2}{dt^2}\vec{x} + \omega_0^2\vec{x} = 0$$

Its general solution has the form

$$\vec{x}(t) = \vec{x}_0 e^{i\omega_0 t} = \vec{x}_0 \cos(\omega_0 t) + \vec{v}_0 \omega_0^{-1} \sin(\omega_0 t)$$

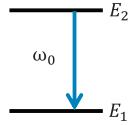
where $\vec{x}_0$ and $\vec{v}_0$ are the initial displacement vector and the initial velocity of the electron, respectively. According to classical electromagnetic theory, the oscillating dipole radiates electromagnetic energy at the following rate:

$$\frac{dE}{dt} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{2}{3c^3}\frac{d^2}{dt^2}\vec{d}$$

where $\vec{d} = e\vec{x}$ is an electric dipole moment, and E is the energy of the oscillating dipole. Accounting for the relation for $\vec{x}(t)$, one can present the radiation rate as

$$\frac{dE}{dt} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{e^2}{3c^3}(\omega_0^4 \vec{x}_0{}^2 + \omega_0^2 \vec{v}_0{}^2) = -\left(\frac{1}{4\pi\varepsilon_0}\right)\frac{2e^2\omega_0^2}{3mc^3}E$$

In this relation, the radiation rate has been averaged over times much larger than ω_0^{-1}.



In quantum theory, spontaneous decay of an excited atom from energy level E_2 to energy level E_1 is accompanied by a photon generation with energy $\hbar\omega_0 = E_2 - E_1$. To bring the **spontaneous emission rate** A_{21} into numerical agreement with the classical radiation rate, a factor f (the **oscillator strength**) must be introduced as follows:

$$A_{21} = \left(\frac{1}{4\pi\varepsilon_0}\right)\frac{2e^2\omega_0^2}{mc^3}f \text{ (the Einstein } A \text{ coefficient)}$$

where f is a measure of the "strength" of the transition.

Classical Oscillator Absorption

Newton's law of motion for an electron oscillator in a field of a linearly polarized monochromatic plane wave is

$$\frac{d^2}{dt^2}\vec{x} + 2\beta\frac{d}{dt}\vec{x} + \omega_0^2\vec{x} = \hat{\varepsilon}\frac{e}{m}E_0 e^{-i(\omega t - kz)}$$

where $\hat{\varepsilon}$ is a unit vector, and $\beta = b/2m$, where b is the **friction coefficient**. The solution of this equation is

$$\vec{x}(t) = \mathrm{Re}\left[\frac{\hat{\varepsilon}(e/m)E_0 e^{-i(\omega t - kz)}}{\omega_0^2 - \omega^2 - i2\beta\omega}\right]$$

The absorption of the applied field changes the oscillator energy. The rate of the field absorption can be considered as the rate at which work is done by the field on the oscillator. It can be presented as

$$\frac{dE}{dt} = \hat{\varepsilon}eE_0\cos(\omega t - kz)\frac{d}{dt}\vec{x}(t)$$

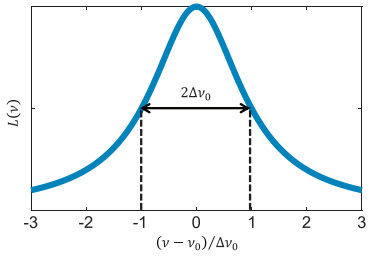
Considering the relation for $\vec{x}(t)$ and averaging over times that are large compared to ω^{-1}, one can obtain the **cycle-averaged rate**:

$$\frac{dE}{dt} = \frac{e^2}{m}E_0^2\frac{1}{\beta}\left[\frac{\beta^2\omega^2}{(\omega_0^2 - \omega^2)^2 + 4\beta^2\omega^2}\right]$$

Frequency detuning $|\omega_0 - \omega| \gg \beta$ results in a very small change in the oscillator energy, i.e., low absorption. If the field frequency ω is close to ω_0, one can use the approximation $\omega_0 + \omega \approx 2\omega_0$ and present the relation as

$$\frac{dE}{dt} \approx \frac{e^2}{4mc\varepsilon_0}I_\nu L(\nu), \quad \text{where} \quad L(\nu) = \frac{1}{\pi}\frac{\Delta\nu_0}{(\nu - \nu_0)^2 + \Delta\nu_0^2}$$

where $I_\nu = c\varepsilon_0 E_0^2/2$ is the field intensity, $L(\nu)$ is the **Lorentzian function**, $\nu = \omega/2\pi$, $\Delta\nu_0 = \beta/2\pi$ is the **half width at half-maximum** (HWHM), and $2\Delta\nu_0$ is the **full width at half-maximum** (FWHM).



Light Absorption

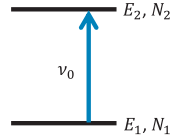
Let us consider light absorption using classical and quantum theories. In the classical absorption theory, the **absorption oscillator rate** can have the shape $S(\nu)$, which is different from the Lorentzian function. In this case, the **rate of energy absorption** by the oscillating dipole is

$$\frac{dE}{dt} = \frac{e^2}{4mc\varepsilon_0} I_\nu S(\nu), \quad \text{where} \quad \int_0^\infty S(\nu)d\nu = 1$$

E is the energy of the oscillating dipole.

Consider a quantum system that consists of N similar atoms. It includes N_2 atoms at the excited energy level E_2 and $N_1 = N - N_2$ atoms at the lower energy level E_1. Here, N_2 and N_1 are referred to as the populations of the E_2 and E_1 levels, respectively. In the quantum approach, the rate of energy absorption must be proportional to the change in population of the lower energy state, dN_1/dt, from which the absorption proceeds. Equating the rates of energy absorption in the classical and quantum approaches, one can obtain the relation

$$\frac{dE}{dt} = -h\nu_0 \frac{dN_1}{dt}$$



From this relation, we can obtain the rate of change in the population of the lower energy state caused by absorption. This rate of change has the form

$$\frac{dN_1}{dt} = -A_{21} \frac{c^2}{8\pi h\nu_0^3} N_1 I_\nu S(\nu)$$

We have considered absorption of **narrowband** radiation. In the case of **broadband** light, this relation takes the form

$$\frac{dN_1}{dt} = -A_{21} \frac{N_1}{8\pi h} \int_0^\infty \frac{c^2}{\nu^3} I(\nu) S(\nu) d\nu$$

Here, $I(\nu)d\nu$ is the radiation intensity in the frequency band from ν to $\nu + d\nu$.

Stimulated Emission

The intensity of light can be presented as $I(\nu) = c\rho(\nu)$, where $\rho(\nu)$ is a spectral energy density. Let us consider a system in which the atoms and the radiation are in equilibrium. In this case, $dN_1/dt = 0$ and $dN_2/dt = 0$. The population of the atomic levels must be constant. As evident from quantum statistical mechanics, in thermal equilibrium at temperature T, the populations N_1 and N_2 of the E_1 and E_2 energy levels must satisfy the relation $N_2/N_1 = e^{-h\nu_0/\kappa_B T}$. The spectral energy density of thermal radiation is the **Planck spectrum**, i.e., $\rho(\nu) = u(\nu)$. If the Planck spectrum $u(\nu)$ does not essentially change near ν_0, one can obtain the relation $u(\nu_0) = \frac{8\pi h\nu_0^3}{c^3}\frac{1}{N_1/N_2 - 1}$, which can be presented in the form

$$\frac{A_{21}c^3}{8\pi h\nu_0^3}N_1 u(\nu_0) = A_{21}N_2 + \frac{A_{21}c^3}{8\pi h\nu_0^3}N_2 u(\nu_0)$$

The term on the left side of the last equation describes the rate of absorption. The first term on the right side describes the rate of spontaneous emission. The second term on the right side describes the emission process, which is akin to spontaneous emission, but unlike spontaneous emission, the rate of this emission is proportional to the spectral density of radiation. This emission process is known as **stimulated emission**.

Now we introduce some coefficients:

$$B_{12} = B_{21} = A_{21}\frac{c^3}{8\pi h\nu_0^3} \quad \text{(the Einstein } B \text{ coefficients)}$$

Accounting for these coefficients, we can rewrite the equation for the population of the energy level in the form

$$N_1 B_{12}\rho(\nu_0) = N_2 A_{21} + N_2 B_{21}\rho(\nu_0)$$

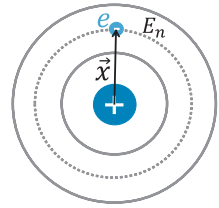
This equation was introduced by Einstein in 1916, more than a decade before the Einstein A and B coefficients could be obtained using the quantum mechanical approach.

Oscillator Strength

Consider the quantum mechanical validation of the classical electron oscillator model. To describe quantum mechanical systems, which are not stationary, we need to use the **time-dependent Schrödinger equation**:

$$i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi$$

If a bound electron at position $\vec{x}$ interacts with light, the Hamiltonian operator of the system, $\hat{H}=\hat{H}_0+\hat{H}_I$, is a sum of the operator $\hat{H}_0=-(\frac{\hbar^2}{2m})\frac{d^2}{dt^2}+V(\vec{x})$, which describes the kinetic and potential electron energy in the nucleus field, and the operator $\hat{H}_I$, which describes the electron–light interaction energy. The electron wavefunction $\psi(\vec{x},t)$ can be presented as



$$\psi(\vec{x},t)=\sum_n a_n(t)\varphi_n(\vec{x})$$

where $\varphi_n(\vec{x})$ are the eigenfunctions of the time-independent Schrödinger equation:

$$\hat{H}_0\varphi_n(\vec{x})=E_n\varphi_n(\vec{x})$$

The functions $\varphi_n(\vec{x})$ are orthogonal, i.e.,

$$\int d^3\vec{x}\varphi_m^*(\vec{x})\varphi_n(\vec{x})=\delta_{mn}$$

where δ_{mn} is the **Kronecker symbol**. $|a_n(t)|^2$ is the probability of finding the electron at time t in the state $\varphi_n(\vec{x})$. All states are nondegenerate. Substituting $\psi(\vec{x},t)$ into the time-dependent Schrödinger equation, one can obtain the system of equations for the amplitides:

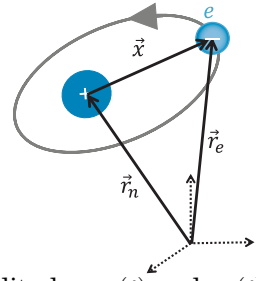
$$i\hbar\frac{da_m(t)}{dt}=E_m a_m(t)+\sum_n V_{mn}a_n(t)$$

where $V_{mn}=\int d^3\vec{x}\varphi_m^*(\vec{x})\hat{H}_I\varphi_n(\vec{x})$ and $\hat{H}_I=-e\vec{x}\cdot\vec{E}$, and where $\vec{d}=e\vec{x}$ is an electric dipole moment.

Oscillator Strength (cont.)

If the electric field wavelength exceeds the atomic dimension, this wavelength can be considered to be independent of the electron position $\vec{x}$, and $V_{mn} = -e\vec{x}_{mn} \cdot \vec{E}(t)$, where

$$\vec{x}_{mn} = \int d^3\vec{x}\varphi_m^*(\vec{x})\vec{x}\varphi_n(\vec{x})$$

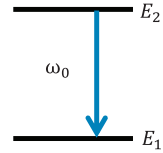


The expectation value of the electron displacement $\vec{x}$ at time t is

$$\langle\vec{x}(t)\rangle = \int d^3\vec{x}\,\vec{x}\,|\psi(\vec{x},t)|^2$$

$$= \sum_m \sum_n \vec{x}_{mn} a_m^*(t) a_n(t)$$

Consider a two-level system. The amplitudes $a_1(t)$ and $a_2(t)$ correspond to a ground state and an excited state, respectively. Accounting for the system of equations for the amplitides, one can obtain the equation for $\langle\vec{x}(t)\rangle$ as follows:



$$\frac{d^2}{dt^2}\langle\vec{x}\rangle + \omega_0^2\langle\vec{x}\rangle = \frac{2e\omega_0}{\hbar}\vec{x}_{12}(\vec{x}_{12}\vec{E})(|a_1(t)|^2 - |a_2(t)|^2)$$

If the electric field is directed along the z axis, we can write $\vec{E} = E\hat{z}$, where $\hat{z}$ is the unit vector, and $\langle z\rangle = \langle\vec{x}\rangle \cdot \hat{z}$. If the light power is weak, the amplitudes $|a_2|^2 \ll 1$ and $|a_1|^2 \approx 1$. In this approximation, the equation for $\langle\vec{x}(t)\rangle$ is

$$\frac{d^2}{dt^2}\langle z\rangle + \omega_0^2\langle z\rangle = \frac{2e\omega_0}{3\hbar}|\vec{x}_{12}|^2 E$$

where $|\vec{x}_{12}|^2$ is the matrix element between states 1 and 2 of the electron coordinate $\vec{x}$. We can compare this equation with Newton's law of motion for the classical oscillator: $\frac{d^2}{dt^2}z + \omega_0^2 z = \frac{e}{m}E$. The two equations match if the right side of the equation for $\langle z\rangle$ is multiplied by a factor

$$\boxed{f = \frac{2m\omega_0}{3\hbar}|\vec{x}_{12}|^2}$$

known as the **oscillator strength**.

The **spontaneous emission rate** is $\boxed{A_{12} = \frac{e^2\omega_0^3}{3\hbar\pi\varepsilon_0 c^3}|\vec{x}_{12}|^2}$

Frictional Processes

Atoms in gases collide with each other. According to the Lorentz atomic model, all orientations of displacements and momenta of atomic electrons are equally probable after a collision. Indeed, each atom is bombarded by other atoms from any direction.

Consider the evolution of the electron displacement of atoms whose collisions occur before time t_1. This consideration will include a large number of collisions (not a single collision). We introduce the **complex displacement** as $\vec{X}(t;t_1) = \vec{x}(t;t_1) + i\vec{p}(t;t_1)/m\omega_0$, where $\vec{x}$ and $\vec{p}$ are the electron displacement and momentum at time t, respectively. Since the displacement and momentum of an electron both vanish, on average, after a collision, $\vec{X}(t_1;t_1) = 0$. The collision-free fraction of atoms in the time interval between t_1 and t is $f(t;t_1)$. After a time δt, this changes as $f(t+\delta t;t_1) = f(t;t_1) - \gamma_c f(t;t_1)\delta t$, or $df/dt = -\gamma_c f$, where γ_c is the collision rate. The solution of this equation is $f(t;t_1) = e^{-\gamma_c(t-t_1)}$. Now we introduce the collision-averaged complex displacement $\bar{\vec{X}}$ as $\bar{\vec{X}}(t) = \int_{-\infty}^{t} \vec{X}(t;t_1)\gamma_c f(t;t_1)dt_1$. Keeping in mind that $\vec{X}(t_1;t_1) = 0$, we obtain Newton's law of motion for an electron oscillator in the form

$$\frac{d\bar{\vec{X}}}{dt} + i(\omega_0 - i\gamma_c)\bar{\vec{X}} = i\hat{\varepsilon}\frac{e}{m\omega_0}\vec{E}$$

from which we obtain

$$\boxed{\frac{d^2\bar{\vec{x}}}{dt^2} + 2\gamma_c\frac{d\bar{\vec{x}}}{dt} + (\omega_0^2 + \gamma_c^2)\bar{\vec{x}} = \hat{\varepsilon}\frac{e}{m}\vec{E}}$$

For optical frequencies, $\omega_0^2 \gg \gamma_c^2$. When the equation for $\bar{\vec{x}}$ is compared with the equation of motion for an electron damping oscillator that absorbs the electromagnetic field, it is apparent that the collision rate is $\gamma_c = \beta$, where $\beta = b/2m$, where b is the friction coefficient. This means that $\gamma_c = 2\pi\Delta\nu_0$, where $\Delta\nu_0$ is the HWHM of the absorption Lorentzian-shaped function. This broadening of the line is associated with collisions and is referred to as **collisional broadening**.

Radiative Broadening

The displacement of an electron oscillating at frequency ω_0 with a damping factor γ_0 can be presented as

$$x \cong x_0 e^{-\gamma_0 t/2} e^{-i\omega_0 t}$$

According to electromagnetic theory, the electric field $E(t)$ radiated by that electron has the same time dependence and can be presented as $E(t) = E_0 e^{-\gamma_0 t/2} e^{-i\omega_0 t}$. This is not an infinite, monochromatic wave. Assume that $t = 0$ is its initial time. The frequency components of the wave can be obtained taking its Fourier transform as

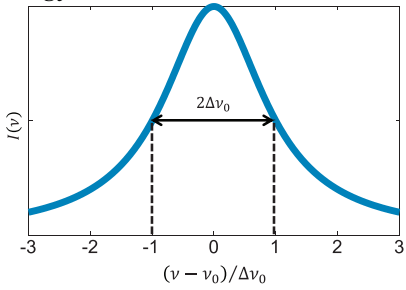
$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} E(t) e^{i\omega t} dt = \frac{E_0}{\sqrt{2\pi}} \int_0^{\infty} e^{i[(\omega-\omega_0)+i\gamma_0/2]t} dt$$

i.e., $E(t) = i \frac{E_0}{\sqrt{2\pi}} \frac{1}{[(\omega-\omega_0)+i\gamma_0/2]}$

Considering that $\gamma_0 \ll \omega$ for optical frequencies, one can obtain the **intensity distribution** as

$$I(\omega) = I_0^{\omega} \frac{\gamma_0/2\pi}{(\omega-\omega_0)^2 + \gamma_0^2/4}, \quad \text{or} \quad I(\nu) = I_0^{\nu} \frac{1}{\pi} \frac{\Delta\nu_0}{(\nu-\nu_0)^2 + \Delta\nu_0^2}$$

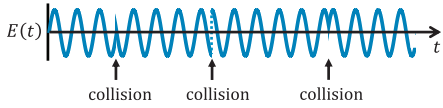
where $I_0^{\omega} = \int_0^{\infty} I(\omega) d\omega$ or $I_0^{\nu} = \int_0^{\infty} I(\nu) d\nu$ is the total intensity of the emission. The intensity is described by the Lorentzian function. Its FWHM is $\Delta\omega_0 = 2(\omega - \omega_0) = \gamma_0 = 4\pi\Delta\nu_0$. According to the uncertainty principle, the energy width ΔE of an atomic level must satisfy the relation $\Delta E \cdot \Delta t \approx \hbar$. If $\Delta t = \tau_0$, where $\tau_0 = 1/A_{21}$ is the radiative lifetime of the level, the energy width of the level is $\Delta E \approx \hbar/\tau_0$ or $\Delta\omega \approx \tau_0^{-1}$. For a ground state and a metastable state, $\gamma_0 \approx 0$. $\Delta\omega$ is the fundamentally smallest possible linewidth (**natural width**) that can be realized experimentally. This broadening is known as homogeneous **natural** or **radiative broadening**. It is associated with spontaneous emission.



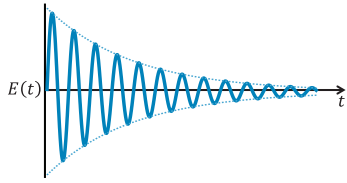
Collisional Broadening

Atoms and molecules in gases collide with each other. Generally, collisions occur between two particles. In solids and liquids, each atom undergoes an interaction with closely located vibrating atoms. These interactions are referred to as **phonon collisions**. All collisions result in a broadening of energy levels (**collisional broadening**).

Elastic collisions, which do not change the energy of atoms, can only interrupt the phase of the oscillations. These are known as **dephasing collisions**. A dephasing collision with an excited atom does not cause the electron to move down from the excited level, nor does it affect the lifetime of the excited level. Broadening caused by dephasing collisions is known as **dephasing broadening** or **T_2 broadening**. T_2 is the average time between dephasing (elastic) collisions. Dephasing broadening can be estimated as $\gamma_c^{(2)} = T_2^{-1}$.



Inelastic collisions change the energy of atoms. These collisions can cause the electron of the excited atom to move down from its excited energy level before its spontaneous decay. This type of collisional broadening is known as **T_1 broadening**. Its decay rate is $\gamma_c^{(1)} = T_1^{-1}$. **Collisional decay** takes place in all types of media. Generally, $T_2 \ll T_1$.



The **linewidth** of any energy level in the system that undergoes collisional broadening can be presented as

$$\Delta\nu_c = \frac{1}{2\pi}\left(A_{21} + \frac{1}{T_1} + \frac{1}{T_2}\right) = \Delta\nu_0 + \frac{1}{2\pi}\left(\gamma_c^{(1)} + \gamma_c^{(2)}\right)$$

Doppler Broadening

Consider a gas with very weak collisions. In thermal equilibrium, its atoms move randomly in all directions with an average velocity $v = \sqrt{8\kappa_B T/m\pi}$, where T is the temperature, m is the mass of the atom, κ_B is the **Boltzmann constant**, and $v = |\vec{v}| \ll c$. The fraction of atoms having velocities between v and $v + dv$ is given by the **Maxwell–Boltzmann distribution**:

$$f(v) = \sqrt{\frac{m}{2\pi\kappa_B T}} \exp\left[-\frac{m}{2\kappa_B T}(v_x^2 + v_y^2 + v_z^2)\right] dv_x dv_y dv_z$$

where v_x, v_y, and v_z are the x, y, and z components of the velocity $\vec{v}$, respectively. As can be seen from the **Doppler effect** (discovered by Christian Doppler in 1842), the frequency shift received by the observer from atoms moving along the x axis toward the observer is $\nu = \nu_0(1 + \frac{v_x}{c})$. Here, ν_0 is the source frequency. The probability $P(\nu)d\nu$ that the transition frequency can be found between ν and $\nu + d\nu$ equals the probability that the velocity component v_x can be found between v_x and $v_x + dv_x$. Considering that $v_x = \frac{c}{\nu_0}(\nu - \nu_0)$ and $d\nu_x = \frac{c}{v_x} d\nu$, one obtains the probability as

$$P(\nu)d\nu = f(\nu)d\nu \iint_{-\infty}^{+\infty} f(v_y, v_z) dv_y dv_z$$

Integrating this relation over all frequencies ν, one obtains

$$P(\nu) = \frac{c}{\nu_0}\sqrt{\frac{m}{2\pi\kappa_B T}} \exp\left[-\frac{mc^2}{2\kappa_B T}\left(\frac{\nu - \nu_0}{\nu_0}\right)^2\right]$$

The intensity of the emission $I(\nu) = I_0 P(\nu)$ is a **Gaussian function**:

$$I(\nu) = \frac{2}{\Delta\nu_D} I_0 \sqrt{\frac{\ln 2}{\pi}} \exp\left[-4\ln 2\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right)^2\right]$$

with the FWHM equal to $\Delta\nu_D = 2\nu_0\sqrt{\frac{2\ln 2\kappa_B T}{mc^2}}$.

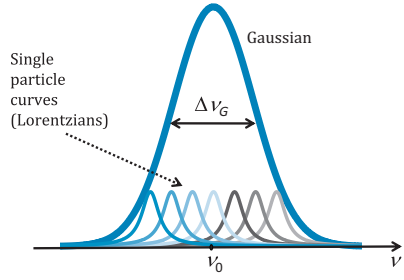
$I_0 = \int_0^\infty I(\nu)d\nu$ is the total emission intensity.

Homogeneous and Inhomogeneous Broadening

Atoms with slightly different numbers of neutrons in their nuclei exhibit small differences in their energy levels, which result in a slight difference in central frequencies of their emission lines (an **isotope shift**). This shift results in **isotope broadening**.

If all atoms have identical opportunities to radiate with equal probability, **homogeneous broadening** takes place in the system. Homogeneous broadening includes radiative (natural) broadening and collisional broadening, both of which can be described with a **Lorentzian line-shape function** $g_L(\nu)$.

For **inhomogeneous broadening**, which can be described with a **Gaussian line-shape function** $g_G(\nu)$, specific portions of atoms contribute to different parts of the emission line shape. However, each atom of the system still radiates with its own natural line shape, which can be described by a Lorentzian function. Inhomogeneous broadening includes Doppler broadening, isotope broadening, and broadening in solids, where active ions experience different local electric and magnetic fields.



Collisional broadening caused by *inelastic* collisions, which is known as T_1 broadening, can decrease the decay time associated with radiative decay; i.e., $\tau_0 = 1/A_{21}$.

Collisional broadening caused by *elastic* collisions (T_2 broadening or dephasing broadening), Doppler broadening, isotope broadening, and broadening in solids does not affect the lifetime.

In general, a spectral line can be characterized by a convolution of $g_L(\nu)$ and $g_G(\nu)$, known as a **Voigt profile**:

$$g_V(\nu) = \int_{-\infty}^{\infty} g_G(\nu')g_L(\nu - \nu')d\nu'$$

Active Media

The concept of using stimulated emission for amplification of EM radiation in the microwave spectrum was developed by Charles Townes, Joseph Weber, Aleksandr Prokhorov, and Nikolay Basov. The first **maser** (**microwave amplification by stimulated emission of radiation**) was demonstrated by James Gordon, Charles Townes, and Herber Zeiger in 1954. In 1957, Gordon Gould proposed using a Fabry–Pérot cavity and introduced the term **laser** (**light amplification by stimulated emission of radiation**), which was first demonstrated by Theodore Maiman in 1960. Lasers can be categorized according to their active media.

- In some active media—such as gases, liquids with dissolved dyes, **rare-earth** (RE)-doped solids, and **transition-metal** (TM)-doped solids—laser cycles, which are based on absorption and stimulated emission of photons, take place in isolated, optically active centers. Absorption and stimulated emission take place between the energy levels of the optically active center.

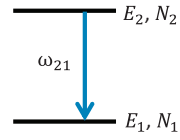
  Optically active centers in solids are (1) **dopant ions** that are *intentionally* created in solids (**hosts**) by various methods, or (2) **lattice defects** (**color centers**) created in crystals *by chance* during the growth process. A variety of interesting optical properties and applications of solids are associated with their optically active centers.

  In the case of RE- or TM-doped solids, the energy levels of the dopant are located within the energy gap of the insulator host. The energy levels of the free-of-host ion are affected by the presence of the next nearest neighbors when this free-of-host ion is doped in the host.

- In other active media, such as semiconductors, the host materials, themselves, are involved in the laser cycles.

  In Raman and Brillouin lasers, which are based on stimulated Raman and Brillouin scattering, respectively, the host materials are involved in the laser cycles, too.

Einstein *A* and *B* Coefficients



Consider a two-level system with energy levels E_1 and E_2. There might be more than one quantum state associated with these energy levels. m_1 and m_2 are labels for the different possible states of energy E_1 and E_2, respectively. $\mathcal{N}_1(m_1)$ and $\mathcal{N}_2(m_2)$ are the populations in these states. N_1 and N_2 are the total populations of the energy levels E_1 and E_2, respectively.

We assume that all states of a given level are equally populated. In this case, $\mathcal{N}_1(m_1)$ and $\mathcal{N}_2(m_2)$ are independent of m_1 and m_2, and equal to E_1/g_1 and E_2/g_2, respectively. Here, g_i is the degeneracy or statistical weight of level i. In this case, the Einstein A coefficient related to the rate of spontaneous emission of light $A_{21} = \frac{1}{g_2}\sum_{m_1,m_2}\mathcal{A}(m_2,m_1)$ is the sum of the spontaneous emission rates $\mathcal{A}(m_2,m_1)$ from m_2 to all possible lower states m_1. Since m_1 and m_2 are nondegenerate states, $\mathcal{A}(m_2,m_1) = \frac{e^2\omega_{21}^3}{3\pi\varepsilon_0\hbar c^3}|\vec{x}_{m_1m_2}|^2$, where $\vec{x}_{m_1m_2}$ is the matrix element between states m_1 and m_2 of the electron coordinate $\vec{x}$, and $\omega_{21} = (E_2 - E_1)/\hbar$.

One can present the **Einstein *A* coefficient** as

$$A_{21} = \frac{1}{g_2}\sum_{m_1,m_2}\frac{e^2\omega_{21}^3}{3\pi\varepsilon_0\hbar c^3}|\vec{x}_{m_1m_2}|^2 = \frac{g_1}{g_2}\frac{2\pi e^2 f_{12}}{\varepsilon_0 mc\lambda_0^2}$$

where $f_{12} = \frac{1}{g_1}\frac{2m\omega_{21}}{3\hbar}\sum_{m_1,m_2}|\vec{x}_{m_1m_2}|^2$ is the oscillator strength for absorption. f_{21} is the oscillator strength for emission:

$$f_{21} = -\frac{g_1}{g_2}f_{12}$$

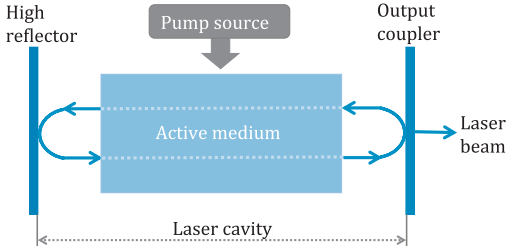
B_{21} and B_{12} are the **Einstein *B* coefficients** responsible for induced photon emission and absorption, respectively:

$$B_{21} = \frac{c^3}{8\pi h\nu_{21}^3}A_{21} \quad \text{and} \quad B_{12} = \frac{g_2}{g_1}B_{21}$$

$\tau_r = 1/A_{21}$ is the **radiative lifetime** of energy level E_2.

Solid-State Laser Operation

Solid-state lasers can be divided into two major classes: (1) lasers with insulating host materials containing optically active centers and (2) semiconductor lasers. Historically, lasers with semiconductor hosts are known as semiconductor lasers. The term solid-state laser is applied to lasers that are based on optically active centers in insulator host materials.

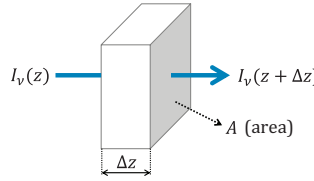


To operate as a solid-state laser, the physical system must include the **active material** (also known as the **laser material**), which is placed in an optical resonator. The resonator includes a high reflector and an output coupler. This active material must be pumped with an external source of energy. The operation of the system is based on three functions: energy absorption, energy storage, and energy extraction in a coherent light form.

The active material absorbs the excitation energy and reemits photons in the stimulated emission process at the laser wavelength. These photons circulate in the laser cavity and experience gain each time they pass through the pumped laser material. A portion of these photons passes through the output coupler, producing the laser beam.

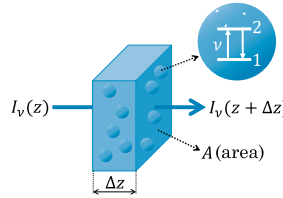
A small amount of spontaneous emission (also known as noise radiation) at the laser transition frequency propagates along the device axis. This emission builds the amplified laser signal. If the total **round-trip gain**, which includes laser gain and cavity losses, is greater than unity, the threshold condition is reached. In this system, the noise radiation grows exponentially with each successive round trip into a coherent, self-sustained oscillation inside the laser cavity. In a steady state, the recirculating signal neither grows nor decays on each round trip, and the total round-trip gain exactly equals unity.

Absorption and Stimulated Emission Cross Sections



Consider a beam with intensity $I_\nu(z)$ propagating in the z direction. The rates at which the beam passes through an area A at z and $z+\Delta z$ are $I_\nu(z)A$ and $I_\nu(z+\Delta z)A$, respectively. The rate at which EM energy leaves the volume $A\Delta z$ is $\frac{\partial}{\partial t}(u_\nu A\Delta z) = -\frac{\partial(I_\nu A)}{\partial z}\Delta z$. Here, we have accounted for the fact that $[I_\nu(z+\Delta z) - I_\nu(z)]A \approx \frac{\partial(I_\nu A)}{\partial z}\Delta z$. Because the field energy density $u_\nu = I_\nu/c$, we can obtain the equation

$$\frac{1}{c}\frac{\partial I_\nu}{\partial t} + \frac{\partial I_\nu}{\partial z} = 0 \quad (\text{the } \textbf{equation of continuity})$$



The wave propagation between z and $z+\Delta z$ takes place in the medium, which includes N_1 atoms per unit volume in the lower energy level of the resonance transition. N_2 is the number of atoms per unit volume in the upper level. The rate of change of the energy per unit volume in the medium as a result of absorption and stimulated emission is

$$h\nu\frac{dN_2}{dt} = -\frac{h\nu}{c}I_\nu S(\nu)B_{21}\left(N_2 - \frac{g_2}{g_1}N_1\right)$$

The equation for the intensity I_ν takes the form

$$\frac{1}{c}\frac{\partial I_\nu}{\partial t} + \frac{\partial I_\nu}{\partial z} = \sigma_{21}(\nu)\left(N_2 - \frac{g_2}{g_1}N_1\right)I_\nu$$

where $\sigma_{21}(\nu) = h\nu\frac{B_{21}u_\nu}{I_\nu}S(\nu)$ is the **stimulated emission cross section**. $\sigma_{12}(\nu) = \frac{g_2}{g_1}\sigma_{21}(\nu)$ is the **absorption cross section**. There is no geometrical object associated with the cross section. It can be treated as an effective area associated with the atomic transition. Every photon in this area will "force" an atom to undergo absorption or stimulated emission.

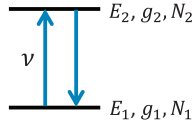
Absorption and Gain Coefficients

In the temporal steady state, I_ν is independent of time. The equation for the intensity takes the form

$$\frac{\partial I_\nu}{\partial z} = g(\nu) I_\nu$$

where

$$g(\nu) = \sigma_{21}(\nu)\left(N_2 - \frac{g_2}{g_1}N_1\right)$$



The solution of this equation is

$$I_\nu(z) = I_\nu(0)e^{g(\nu)z}$$

where $I_\nu(0)$ is the input intensity. The value

$$\Delta N_{21} = \left(N_2 - \frac{g_2}{g_1}N_1\right)$$

describes the **population difference** between the levels with energies E_2 and E_1. If $\Delta N_{21} > 0$, the coefficient $g(\nu)$ describes the exponential intensity growth with a distance z of propagation. $g(\nu)$ is known as the **gain coefficient**. If $\Delta N_{21} < 0$, the intensity exponential decreases with the distance z of propagation. In this case, a coefficient $\alpha(\nu) = -g(\nu)$ can be introduced:

$$\alpha(\nu) = \sigma_{12}(\nu)\left(N_1 - \frac{g_1}{g_2}N_2\right)$$

$\alpha(\nu)$ is known as the **absorption coefficient**. In this case, the equation for the intensity is written as

$$\frac{\partial I_\nu}{\partial z} = -\alpha(\nu) I_\nu$$

Its solution is

$$I_\nu(z) = I_\nu(0)e^{-\alpha(\nu)z} \quad \text{(the Beer–Lambert law)}$$

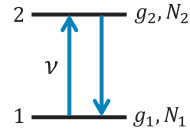
$N = N_1 + N_2$ is the total population density. For low excitation ($N_2 \ll N_1$), one can obtain the widely used approximation called the **small-signal absorption coefficient**:

$$\alpha_0(\nu) \approx \sigma_{12}(\nu)N$$

Population Inversion

Amplification can occur only if the gain coefficient $g(\nu) > 0$. This is possible when the population difference $\Delta N_{21} > 0$; that is,

$$N_2 > \frac{g_2}{g_1} N_1$$



If the upper level is more populated than the lower level, a **population inversion** takes place in the system. Population inversion is a **necessary condition for amplification** or **lasing**. Here we assume for simplicity that $g_2/g_1 = 1$. The population of the upper level can be increased by absorption of photons from the pump beam. Increasing the input light intensity, one might expect the entire population to be transferred from level 1 to level 2. This is not the case in a two-level system. The absorption coefficient becomes smaller and smaller as the pump intensity I_ν increases: $\alpha(\nu) = \sigma_{12}(\nu)(N_1 - N_2) \approx \frac{\alpha_0(\nu)}{1+I_\nu/I_\nu^{\text{sat}}}$, where I_ν^{sat} is the saturation intensity. Indeed, the level populations N_1 and N_2 can change due to absorption, stimulated emission, and spontaneous emission. The change in populations can be described using the **rate equations** as follows:

$$\frac{dN_2}{dt} = -\frac{\sigma_{21}(\nu)}{h\nu} I_\nu (N_2 - N_1) - A_{21} N_2$$

$$\frac{dN_1}{dt} = \frac{\sigma_{21}(\nu)}{h\nu} I_\nu (N_2 - N_1) + A_{21} N_2$$

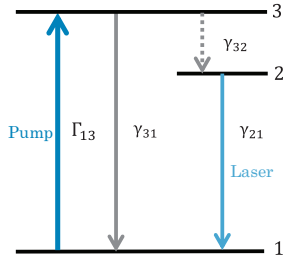
The steady-state solutions can be obtained by setting the time derivatives equal to zero ($d/dt = 0$) as follows:

$$N_2 = \frac{I_\nu/I_\nu^{\text{sat}}}{1+2I_\nu/I_\nu^{\text{sat}}} N, \text{ and } N_1 = \frac{1+I_\nu/I_\nu^{\text{sat}}}{1+2I_\nu/I_\nu^{\text{sat}}} N, \text{ where } I_\nu^{\text{sat}} = \frac{h\nu A_{21}}{\sigma_{21}(\nu)}$$

is the **saturation intensity**, i.e., the intensity at which the stimulated emission rate equals the spontaneous decay rate. If $I_\nu \gg I_\nu^{\text{sat}}$, the populations become $N_2 \approx N_1 \approx N/2$.

It is impossible to attain a population inversion in a two-level system.

Three-Level Laser Scheme



Consider a **three-level laser system**, where the laser transition occurs between level 2 and level 1 (the ground state). We will assume that the system is in thermal equilibrium before pumping from level 1 to level 3 at the rate Γ_{13}. γ_{31}, γ_{32}, and γ_{21} are the decay rates between levels 3 and 1, levels 3 and 2, and levels 2 and 1, respectively. These rates include both the radiative decay rate and a collisional decay rate; i.e., $\gamma_{ij} = \gamma_{ij}^{\text{rad}} + \gamma_i^{\text{coll}}$, where $\gamma_{ij}^{\text{rad}} = A_{ij}$, and $\gamma_i^{\text{coll}} = 1/T_1^{(i)}$, where $T_1^{(i)}$ is the collisional decay time from level i. For laser materials, the decay for level 2 must be predominantly radiative; i.e., $\gamma_{21} \approx A_{21}$. The rate equations for the population of levels 1, 2, and 3 are

$$\frac{dN_1}{dt} = -\Gamma_{13}N_1 + \gamma_{21}N_2 + \gamma_{31}N_3$$

$$\frac{dN_2}{dt} = -\gamma_{21}N_2 + \gamma_{32}N_3$$

$$\frac{dN_3}{dt} = \Gamma_{13}N_1 - (\gamma_{31} + \gamma_{32})N_3$$

The total population is $N = N_1 + N_2 + N_3$. To find steady-state solutions of these equations, we need to set all time derivatives equal to zero. In this case, the population of the upper (level 2) N_2 and lower (level 1) N_1 laser levels have the forms

$$N_2 = \frac{\gamma_{32}\Gamma_{13}}{\gamma_{21}(\gamma_{31}+\gamma_{32})+(\gamma_{21}+\gamma_{32})\Gamma_{13}}N, N_1 = \frac{\gamma_{21}(\gamma_{32}+\gamma_{31})}{\gamma_{21}(\gamma_{31}+\gamma_{32})+(\gamma_{21}+\gamma_{32})\Gamma_{13}}N$$

A **population inversion** can occur if $\frac{N_2}{N_1} = \frac{\gamma_{32}\Gamma_{13}}{\gamma_{21}(\gamma_{32}+\gamma_{31})} > 1$ or $\Gamma_{13} > \gamma_{21}(1 + \gamma_{31}/\gamma_{32})$. If we want to minimize the pumping rate Γ_{13}, the ratio γ_{31}/γ_{32} must be as small as possible; i.e., the decay rate from level 2 to level 1 must be very fast compared to the decay rate from level 3 to level 1. If $\gamma_{31}/\gamma_{32} \ll 1$, we can write

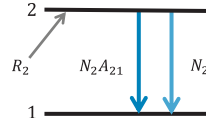
$$\boxed{\Gamma_{13} > A_{21}}$$

This condition is satisfied when a population inversion between levels 2 and 1 can be attained.

Gain Saturation

Assume that a population inversion occurs in a medium; i.e., $\Delta N_{21} = N_2 - \frac{g_2}{g_1} N_1 > 0$. For simplicity, $g_2/g_1 = 1$. The rate equation for the upper level has the form

$$\frac{dN_2}{dt} = R_2 - N_2\left(A_{21} + \frac{B_{21}}{c} I_\nu\right)$$



where R_2 is a pumping flux, i.e., the number of excitations per unit volume per unit time. The steady-state solution of this equation is

$$N_2 = \frac{R_2}{A_{21} + \frac{B_{21}}{c} I_\nu} = \frac{N_2^0}{1 + \frac{I_\nu}{I_\nu^{\text{sat}}}}$$

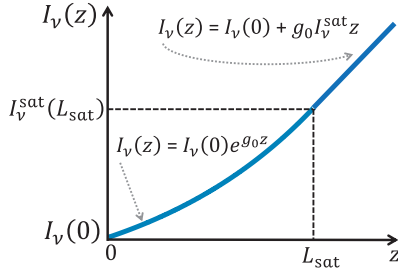
where $N_2^0 = R_2/A_{21}$ is the population of the upper level if $I_\nu = 0$. The gain $g_0 = \sigma_{21}(\nu)\Delta N_{21}^0$ is the **small-signal gain**.

If the intensity I_ν is low ($I_\nu \ll I_\nu^{\text{sat}}$), the developing beam has little effect on the population N_2. When the beam intensity approaches the **saturation intensity** ($I_\nu \approx I_\nu^{\text{sat}}$), the stimulated emission rate becomes as large as the spontaneous emission rate. The beam intensity begins to *deplete* the population N_2. The population difference and gain have the forms

$$\Delta N_2 = \frac{\Delta N_2^0}{1 + \frac{I_\nu}{I_\nu^{\text{sat}}}} \quad \text{and} \quad \boxed{g = \frac{g_0}{1 + \frac{I_\nu}{I_\nu^{\text{sat}}}}}$$

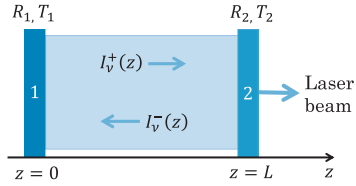
respectively. The length of the medium where saturation intensity occurs is the **saturation length** L_{sat}. A beam grows exponentially over the length L_{sat}.

If $I_\nu \gg I_\nu^{\text{sat}}$, the stimulated emission rate dominates, and the equation $\frac{\partial I_\nu}{\partial z} = gI_\nu$ can be approximated as $\frac{\partial I_\nu}{\partial z} = g_0 I_\nu^{\text{sat}}$. Its solution is $I_\nu(z) = I_\nu(0) + g_0 I_\nu^{\text{sat}} z$.



Laser Threshold Gain

Laser operation is based on stimulated emission. The number of laser cavity photons generated with stimulated emission can be decreased by loss effects, which include scattering, absorption of radiation at the mirrors, and output coupling of radiation. To achieve laser oscillation, amplification based on stimulated emission must overcome all cavity losses. The minimum gain coefficient required to achieve laser oscillation is called the **laser threshold condition**. Ordinarily, the background absorption of radiation within the laser medium is quite small compared with the mirror losses.



Consider a laser in which the gain medium with refractive index $n \approx 1$ fills the entire distance L between the mirrors. R_i and T_i are the reflection and transmission coefficients of mirror i, where $i = 1, 2$. $R_i + T_i = 1$. $I_\nu^\pm(z)$ are the intensities of the beams propagating from mirror 1 to mirror 2 $(+)$ and from mirror 2 to mirror $1(-)$, respectively. At $z = L$, a beam of intensity $I_\nu^+(L)$ incident on mirror 2 is transformed into a reflected beam of intensity $I_\nu^-(L) = R_2 I_\nu^+(L)$. Similarly, at mirror 1 $(z = 0)$, we have $I_\nu^+(0) = R_1 I_\nu^-(0)$. We now consider steady-state [or **continous-wave** (CW)] laser operation. Near the laser threshold, the beam intensities change according to the relations

$$\frac{dI_\nu^\pm}{dz} = \pm g(\nu) I_\nu^\pm, \text{ which have the solutions}$$

$$I_\nu^+(z) = I_\nu^+(0) e^{g(\nu)z} \quad \text{and} \quad I_\nu^-(z) = I_\nu^-(0) e^{[g(\nu)(L-z)]}$$

From the relation $I_\nu^+(0) = R_1 I_\nu^-(0)$, one can obtain $I_\nu^+(0) = R_1 R_2 e^{2\, g(\nu) L} I_\nu^+(0)$. If $I_\nu^+(0) \neq 0$, we have

$$R_1 R_2 e^{2\, g(\nu) L} = 0 \text{ or } \boxed{g_{th}^l = -\frac{\ln(R_1 R_2)}{2L} \text{ (the laser threshold gain)}}$$

If $R_1 R_2 \approx 1$ (high reflectivities), $\boxed{g_{th}^l \approx \frac{(1 - R_1 R_2)}{2L}}$

Optical Bloch Equations

Here we describe the interaction of light with a two-level electron system using the **density matrix approach**. The time evolution of the density matrix can be described by the **Liouville equation**:

$$\boxed{\frac{\partial \rho}{\partial t} = \frac{i}{\hbar}[\rho, \hat{H}]} \quad \text{where} \quad \hat{H} = \hat{H}_0 + \hat{H}_I, \quad \text{and}$$

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{21} \\ \rho_{12} & \rho_{22} \end{pmatrix}, \qquad \hat{H}_0 = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}, \qquad \hat{H}_I = \begin{pmatrix} 0 & -E\mu_d \\ -E\mu_d & 0 \end{pmatrix}$$

are the density matrix (ρ), the unperturbed Hamiltonian ($\hat{H}_0$), and the perturbing Hamiltonian ($\hat{H}_I = e\vec{x} \cdot \vec{E} = -E\hat{\mu}$), respectively. Here, $\vec{E} = \hat{\varepsilon}E = \hat{\varepsilon}E_0 \cos(\omega t)$ is the applied electric field, and

$\hat{\mu} = \begin{pmatrix} 0 & \mu_d \\ \mu_d & 0 \end{pmatrix}$ is the electric dipole operator with matrix elements $\mu_{12} = \mu_{21} = \mu_d = -e(\vec{x}_{21} \cdot \hat{\varepsilon})$.

Using the Liouville equation and taking into account the RWA, one can obtain the following system of equations, called the **optical Bloch equations**:

$$\boxed{\begin{aligned} \frac{d}{dt}(\rho_{11} - \rho_{22}) &= i\frac{\mu_d}{\hbar}E_0(\beta_{21} - \beta_{21}^*) - \frac{(\rho_{11} - \rho_{22}) - (\rho_{11} - \rho_{22})_0}{T_1} \\ \frac{d}{dt}\beta_{21} &= i(\omega - \omega_0)\beta_{21} + i\frac{\mu_d}{2\hbar}E_0(\rho_{11} - \rho_{22}) - \frac{\beta_{21}}{T_2} \end{aligned}}$$

where $\beta_{21}(t) = \rho_{21}(t)e^{i\omega t}$.

In deriving the second equation of this system, we postulate that the term ρ_{21}/T_2 must be added in order to account for the dephasing process in the system, which gives rise to an exponential settling of any off-diagonal element to zero with some time constant T_2 (a **transverse relaxation**).

From the first equation, we see that, in the absense of an optical field $\vec{E}$, the fractional population difference will exponentially settle to its equillibrium value $(\rho_{11} - \rho_{22})_0$ with a time constant T_1 (a **longitudinal relaxation**).

The Bloch Sphere

If the time during which the electromagnetic field applied to a two-level atomic system is short compared to T_1 and T_2, one can ignore the damping terms in the optical Bloch equations. Let us denote the following:

$$w = \rho_{22} - \rho_{11}$$

$$v = i(\beta_{21} - \beta_{12})$$

$$u = \beta_{21} + \beta_{12}$$

In this case, the **optical Bloch equations** are written as

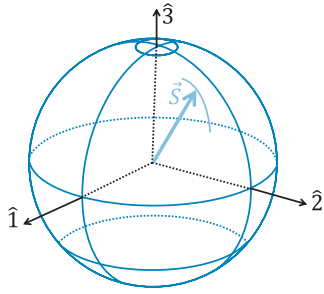
$$\frac{dw}{dt} = -\chi v$$

$$\frac{du}{dx} = \Delta v$$

$$\frac{dv}{dt} = -\Delta u + \chi w$$

where Δ is the detuning. These equations can be interpreted with a **Bloch vector**, which is also known as a **pseudo-spin vector**:

$$\vec{S} = \hat{1}u + \hat{2}v + \hat{3}w$$



where $\hat{1}$, $\hat{2}$, and $\hat{3}$ are mutually orthogonal unit vectors. $S^2 = \vec{S} \cdot \vec{S} = 1$; i.e., the Bloch vector lies on the surface of a unit sphere (the **Bloch sphere**). Now we introduce

$$\vec{Q} = -\hat{1}\chi - \hat{3}\Delta$$

which is known as a **torque vector** (or **axis vector**). Using the pseudo-spin and torque vectors, one can present the system of optical Bloch equations with variables w, v, u as

$$\frac{d\vec{S}}{dt} = \vec{Q} \times \vec{S}$$

The Bloch Sphere (cont.)

From this equation, the time evolution of the density matrix can be presented as a change in the orientation of the Bloch vector.

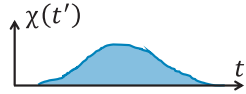
When $\vec{S}$ points straight up, $w = 1$. In this case, $\rho_{22} = 1$ and $\rho_{11} = 0$. The atomic population is entirely in the upper level. When $\vec{S}$ points straight down, $w = -1$. In this case, $\rho_{22} = 0$ and $\rho_{11} = 1$. The atomic population is entirely in its lower energy level.

At resonance ($\Delta = 0$), $\vec{Q} = -\hat{1}\chi$; i.e., the dynamic evolution includes only rotation about the $\hat{1}$ axis. We now present v and w as $v = -\sin\Theta$ and $w = -\cos\Theta$. In this case, from the first equation of the Bloch system, we have

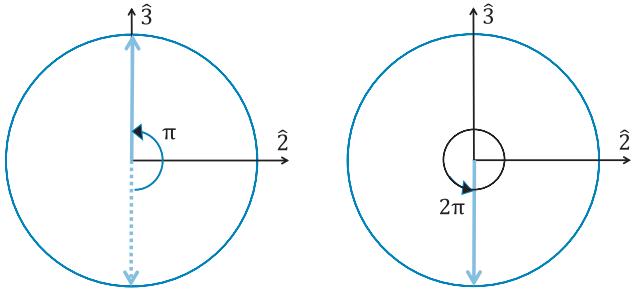
$$\frac{d\Theta}{dt} = \chi \text{ and } \Theta(t) = \chi t$$

If the Rabi frequency is a time function, i.e., the amplitude of the electric field $E_0(t)$ changes with time (light pulses), we write $\Theta(t) = \int_0^t \chi(t')dt'$ (the **area of the pulse**).

The following points are important:

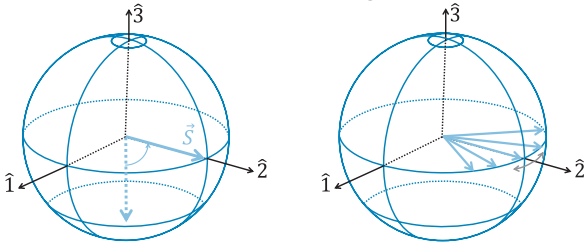


- A **π pulse** $[\Theta(t) = \pi]$ inverts the atomic population from the lower energy level to the upper energy level.
- A **2π pulse** (as well as **$4\pi, 6\pi, \ldots$ pulses**) at the resonance frequency ($\Delta = 0$) returns the atom to its initial state. These pulses have no net effect on the atom.

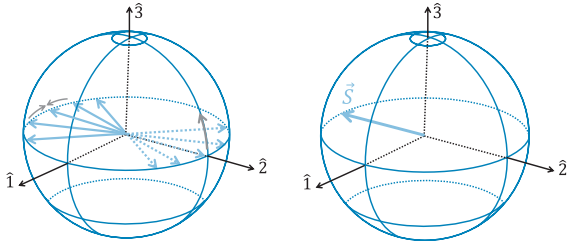


Photon Echo

A photon echo occurs when a collection of atoms (ions) with inhomogeneously broadened absorption lines interacts with several very short (compared to the system coherence time) optical pulses. Before the first pulse, all atoms of the system are assumed to be in their ground states.



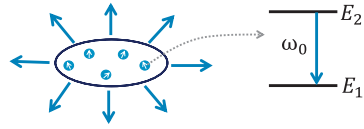
The first $\pi/2$ pulse transforms the atoms in a superposition of the ground and excited states, and all atoms have Bloch vectors pointing along the $\hat{2}$ axis in the **Bloch sphere**. After this first pulse, the atoms evolve freely. As can be seen from the relations for $c_1(t)$ and $c_2(t)$, given on page 51 in the Rabi frequency explanation, the atoms with absorption frequencies $\omega_0 > \omega$, where ω is the laser frequency, will acquire a positive phase that is proportional to the detuning Δ. The atoms with $\omega_0 < \omega$ will attain a negative phase. Their **Bloch vectors** will spread outward in the $\hat{1}\,\hat{2}$ plane.



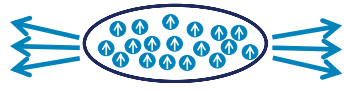
After the second π pulse, all atoms will be in the $\hat{1}\,\hat{2}$ plane, but with a sign change of the $\hat{2}$ component. Now, freely evolving atoms will acquire phases that differ from the laser frequency ω, depending on their transition frequencies ω_0. At a certain time after the second pulse (equal to the time between the first two pulses), the Bloch vectors for all atoms will be aligned along the negative direction of the $\hat{2}$ axis. A macroscopic dipole moment is created that leads to a coherent burst of light known as a **photon echo**.

Collective Spontaneous Emission

In 1954, Robert Dicke predicted cooperative emission from a dense, excited two-level system. Rodolfo Bonifacio and Luigi Lugiato considered this emission as occurring in two distinct forms: **Dicke superradiance** (SR) and **superfluorescence** (SF). Dicke himself never mentioned SF. Consider an ensemble of N_0 two-level atoms confined in a region of space with volume V smaller than $\sim\lambda_0^3$, where $\lambda_0 = 2\pi c/\omega_0$ is the wavelength corresponding to the level separation. The characteristic distance between the atoms is $l = n^{-1/3}$, where $n = N_0/V$ is the density. The value of $\tau_p = l/c$ is the time it takes for radiation to travel between two atoms in the system.



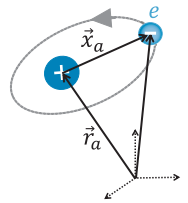
At *low densities*, with $T_1 < \tau_p$, where T_1 is the **spontaneous decay time** of an isolated atom, the atoms do not interact with each other. Each excited atom radiates independently. The spontaneous emission (SE) intensity of the atomic ensemble is $I_{SE} \sim NI_0$, where $I_0 = \hbar\omega_0/T_1$ is the intensity of the radiation of an isolated atom with a decay rate T_1^{-1}. Here, N is the number of excited atoms in the system. SE *isotopically* propagates in all directions.



At *high densities*, with $T_1 \gg \tau_p$, spontaneously radiated atoms reside in the field of the spontaneous radiation created by other atoms. Consider a system that is free from collisions between atoms over a time T_1. After interaction with a π pulse, this system will be a completely inverted two-level system with a macroscopic dipole, which undergoes **collective spontaneous emission** in a time $\tau_c = T_1/N$. The emitted radiation (known as Dicke SR) becomes *anisotropic*. It appears in the direction of the largest thickness of the sample as a short, powerful burst with intensity $I \sim N^2 I_0$. In the case of SF, an initially *incoherent* system spontaneously builds up a macroscopic dipole.

Spontaneous Radiation and Superradiance

Following the classical (Lorentzian) model of atoms, let us consider N charges e with mass m at points with coordinates $\vec{r}_a + \vec{x}_a$ attached to springs with stiffness k_{sp}. The other ends of the springs, which host compensating charges $-e$, are fixed at points $\vec{r}_a$. The dipole moments of the atoms are



$$\vec{d}_a = e\vec{x}_a = e\vec{\tilde{x}}_a \cos(\omega_0 t + \varphi_a)$$

where $\vec{\tilde{x}}_a$ and φ_a are the amplitudes and phases, respectively. $\omega_0 = \sqrt{k_{sp}/m}$ is the frequency corresponding to the level separation. Taking the RWA into account, one can obtain the intensity of radiation:

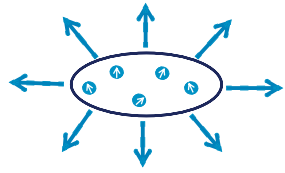
$$I = \frac{2}{3c^3}\left(\frac{d^2\vec{D}}{dt^2}\right)^2 = I_1 + I_2$$

where $\vec{D} = \sum_{a=1}^{N} \vec{d}_a$ is the dipole moment of the system.

$$I_1 = \frac{2}{3c^3}\sum_a \left\langle \left(\frac{d^2\vec{d}_a}{dt^2}\right)^2 \right\rangle$$

$$I_2 = \frac{2}{3c^3}\sum_{a\neq b} \frac{e^2\omega_0^4}{2}(\vec{\tilde{x}}_a \cdot \vec{\tilde{x}}_b)\cos(\varphi_a - \varphi_b)$$

If the amplitudes $\vec{\tilde{x}}_a$ and phases φ_a of different dipoles (atoms) are *not correlated* and vary at random from one atom to another, then $I_2 \ll I_1$ and $I \approx I_1 \propto N$ (**spontaneous radiation**).



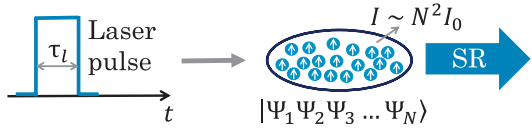
If there is a *correlation* between the amplitudes $\vec{\tilde{x}}_a$ and phases φ_a of different dipoles (atoms), then $I_2 \gg I_1$, and $I \approx I_2 \propto N^2$. This system emits **superradiance** (SR).

Superradiance Compared with Superfluorescence

Superradiance (SR) includes two steps:

1) Excitation of a system, which has slow dephasing processes, by an applied laser pulse results in the formation of a macroscopic dipole (a macroscopic quantum coherent state). The system can be described by a single wavefunction of indistinguishable particles $|\Psi_1\Psi_2\Psi_3\ldots\Psi_N\rangle$.

2) Spontaneous decay of the macroscopic dipole occurs with a rate $\sim NT_1^{-1}$. This decay is accompanied by coherent collective spontaneous emission of a pulse with peak intensity $I \sim N^2 I_0$ and width $\tau_c = T_1/N$.

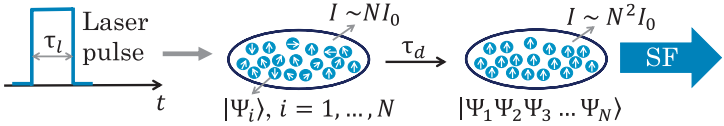


Superfluorencence (SF) occurs when the atoms are initially *incoherent*. Each atom has its own wavefunction $|\Psi_i,\rangle$ $i = 1,\ldots,N$. Phases of individual dipoles (atoms) in the system are then randomly distributed.

1) SF starts with spontaneous emission of the atoms of the system. The radiation intensity is $I \sim NI_0$.

2) Vacuum fluctuations lead to phase synchronization of the dipole moments of the atoms and formation of the macroscopic dipole in the delay time $\tau_d = \tau_c \ln N$.

3) The macroscopic dipole decays superradiantly.



SR and SF are coherent processes. They can be realized only when the decay rate of the macroscopic dipole is larger than any other scattering and relaxation rates in the system. SF is an *intrinsically random* process. Its initial microscopic fluctuations can result in pulse-to-pulse fluctuations in delay time, pulse width, and emission direction.

Self-Induced Transparency

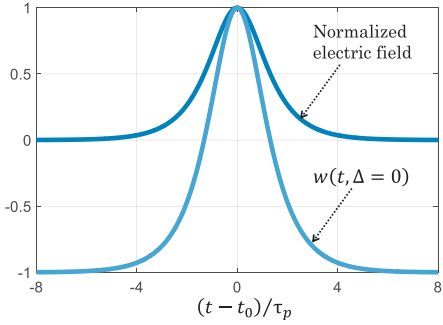
Consider the interaction of two-level atoms with pulses that have pulse durations much shorter than both the population and dipole relaxation times of the atom. The pulse amplitude is $A(t) = \frac{\mu_d}{\hbar} E(t)$. In 1969, Samuel McCall and Erwin Hahn obtained a solution of the optical Bloch equations, presented with variables w, u, v for the system with $\Delta \neq 0$ using the relation $v(t, \Delta) = F(\Delta) v(t, 0)$, where $F(\Delta)$ describes the response of an off-resonance atom. They obtained $F(\Delta) = (1 + \Delta^2 \tau_p^2)^{-1}$ and $A(t) = \frac{\partial \Theta}{\partial t} = \frac{2}{\tau_p} \operatorname{sech}(\frac{t - t_0}{\tau_p})$, where τ_p is the pulse duration, and t_0 is the time at which the amplitude reaches its maximum. The magnitude of the electric field is

$$|E(t)| = \frac{2\hbar}{|\mu_d| \tau_p} \operatorname{sech}\left(\frac{t - t_0}{\tau_p}\right)$$

The total pulse area is $\Theta = \frac{2}{\tau_p} \int_{-\infty}^{+\infty} \operatorname{sech}(\frac{t - t_0}{\tau_p}) dt = 2\pi$. This is a **$2\pi$ pulse**.

The population inversion is $w = -1 + \frac{2}{1 + \Delta^2 \tau_p^2} \operatorname{sech}^2(\frac{t - t_0}{\tau_p})$

A **hyperbolic secant pulse** has a form that allows it to propagate holding its shape and energy. When the electric field increases from $|E| = 0$ to its amplitude $|E| = \frac{2\hbar}{|\mu_d| \tau_p}$, and the probability of finding an atom in the upper state goes from $\rho_{22} = 0$ to $\rho_{22} = (1 + \Delta^2 \tau_p^2)^{-1}$, the pulse induces transparency, giving its energy to atoms during its first half. During its second half, the pulse takes this energy back, and both the pulse amplitude and the probability of finding the excited atom decrease to zero. This effect is known as **self-induced transparency**.



Vector and Scalar Potentials

The six scalar functions $E_{x,y,z}$ and $B_{x,y,z}$ in Maxwell's equations can be replaced by four scalar functions, including three components $A_{x,y,z}$ of the **vector potential** $\vec{A}$ and the **scalar potential** Φ. Indeed, using the relation $\nabla \cdot \vec{B} = 0$ from Maxwell's equation and the vector equation $\nabla \cdot \nabla \times \vec{A} = 0$, one obtains

$$\vec{B} = \nabla \times \vec{A}$$

Using the relation $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$ from Maxwell's equation and the vector equation $\nabla \times \nabla \Phi = 0$, one obtains

$$\vec{E} = -\nabla \Phi - \frac{\partial \vec{A}}{\partial t}$$

Recalling that, at optical frequencies, the magnetic permeability μ of a medium approximately coincides with that of vacuum μ_0 (i.e., $\vec{B} = \mu_0 \vec{H}$), and considering only media with the time invariance of ε, one obtains the following equations, which are equivalent to Maxwell's equations:

$$\nabla^2 \Phi + \frac{\partial}{\partial t}(\nabla \cdot \vec{A}) = -\frac{\rho}{\varepsilon}$$
$$\nabla^2 \vec{A} - \mu_0 \varepsilon \frac{\partial^2}{\partial t^2} \vec{A} = -\mu_0 \vec{J} + \nabla\left(\nabla \cdot \vec{A} + \mu_0 \varepsilon \frac{\partial}{\partial t} \Phi\right)$$

Keep in mind that if one replaces $\vec{A}$ and Φ with $\vec{A}' = \vec{A} + \nabla \Psi$ and $\Phi' = \Phi - \frac{\partial \Psi}{\partial t}$, respectively, the relations for the field vectors $\vec{E}$ and $\vec{B}$ will be unaffected. Ψ is an arbitrary function. In the case of isotropic and homogeneous media, one can require that potentials $\vec{A}$ and Φ obey the **Lorentz gauge** condition:

$$\nabla \cdot \vec{A} + \mu_0 \varepsilon \frac{\partial \Phi}{\partial t} = 0$$

In this case, potentials $\vec{A}$ and Φ satisfy the **nonhomogeneous Helmholtz equations**:

$$\nabla^2 \Phi - \mu_0 \varepsilon \frac{\partial^2 \Phi}{\partial t^2} = -\frac{\rho}{\varepsilon} \quad \text{and} \quad \nabla^2 \vec{A} - \mu_0 \varepsilon \frac{\partial^2 \vec{A}}{\partial t^2} = \mu_0 \vec{J}$$

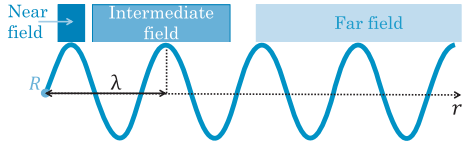
Near Field, Intermediate Field, and Far Field

Here we investigate how electromagnetic waves are generated. Any acceleration of an electric charge creates a changing electric field. Whenever the electric field changes in time, it creates a magnetic field that also changes in time. This created magnetic field generates an electric field, which changes in time, etc. In this way, accelerating charges radiate **electromagnetic waves**.

If all charges of the system are completely at rest with respect to some inertial frame, the system does not radiate. In the real world, no charges are ever completely at rest. Indeed, atoms and electrons of every object are constantly experiencing **thermal motion**. These moving charges radiate electromagnetic waves. The types of radiation and their sources are numerous. Most radiating systems involve a localized oscillating source, which is a system of electric charges and currents that all reside within some finite sphere of radius R such that our observation distance r from the source is external to the source; i.e., $r \gg R$. The currents of oscillating sources can be presented as

$$\vec{J}(\vec{r}, t) = \vec{J}(\vec{r})e^{-i\omega t}$$

In the long-wavelength approximation, $R \ll \lambda = 2\pi c/\omega$, it is common practice to divide the regions of space near the source according to their proximity to the source: near-field, intermediate-field, and far-field regions.



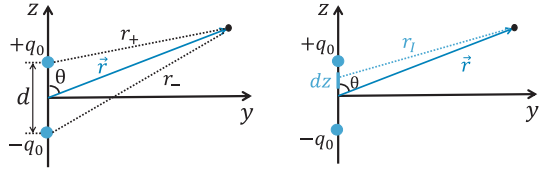
- The **near field** is the region of space that is very far from the source but still much smaller than the wavelength of the light; i.e., $R \ll r \ll \lambda$.
- The **intermediate field** is the region where the observation distance is on the order of the wavelength of the light; i.e., $r \approx \lambda$.
- The **far field** is the region where the observation distance is much greater than the wavelength of the light; i.e., $r \gg \lambda$.

Oscillating Electric Dipole

The simplest way to generate electromagnetic waves is from a system of electric or magnetic dipoles whose moments vary with time. Consider an ideal electric dipole oscillating in time. It consists of two opposite charges, $\pm q_0$, mounted on a spring and separated by a distance d. An **oscillating electric dipole** has the moment

$$\boxed{\vec{p}(t) = p_0 \cos(\omega t)\vec{z}}$$

where $p_0 = q_0 d$ is the maximum value of the dipole moment.



The scalar potential of an electric dipole is written as

$$\Phi(\vec{r}, t) = \frac{1}{4\pi\varepsilon_0}\left[\frac{q_0 \cos[\omega(t - r_+/c)]}{r_+} - \frac{q_0 \cos[\omega(t - r_-/c)]}{r_-}\right]$$

where $r_\mp = \sqrt{r^2 \pm rd\cos\theta + (d/2)^2}$

In the **far-field region** ($r \gg \lambda$), the **scalar potential** has the form

$$\boxed{\Phi(r, \theta, t) \approx -\frac{p_0 \omega}{4\pi\varepsilon_0 c}\left(\frac{\cos\theta}{r}\right)\sin\left[\omega\left(t - \frac{r}{c}\right)\right]}$$

The vector potential is determined by the current:

$$\vec{I}(t) = \frac{dq}{dt}\vec{z} = -q_0 \omega \cos(\omega t)\vec{z}$$

The **vector potential** of an electric dipole has the form

$$\vec{A}(\vec{r}, t) = -\frac{\mu_0}{4\pi}\int_{-d/2}^{d/2} \frac{q_0 \omega \sin[\omega(t - r_I/c)]\vec{z}}{r_I} dz$$

In the far-field region ($r \gg \lambda$), the vector potential has the form

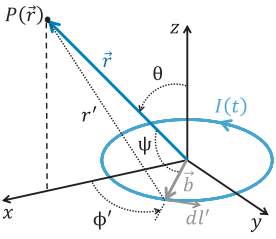
$$\boxed{\vec{A}(r, \theta, t) \approx -\frac{\mu_0 p_0 \omega}{4\pi r}\sin\left[\omega\left(t - \frac{r}{c}\right)\right]\vec{z}}$$

Oscillating Magnetic Dipole

Consider a wire loop of radius b, which supports an alternating current $I(t) = I_0 \cos(\omega t)$. This is the scheme of an **oscillating magnetic dipole**, which has a magnetic dipole moment given as

$$\vec{m}(t) = \pi b^2 I(t)\vec{z} = m_0 \cos(\omega t)\vec{z}$$

where $m_0 = \pi b^2 I_0$ is the maximum value of the dipole moment. The loop is uncharged, so its scalar potential equals zero ($\Phi = 0$).



We place the x axis such that the observation point $P(\vec{r})$ is in the xz plane. The **vector potential** of an oscillating magnetic dipole can be presented as

$$\vec{A}(\vec{r},t) = \frac{\mu_0}{4\pi}\int \frac{I_0 \cos[\omega(t - r'/c)]}{r'} d\vec{l}'$$

where $r' = \sqrt{r^2 + b^2 - 2rb\cos\psi} = \sqrt{r^2 + b^2 - 2rb\sin\theta\cos\phi'}$. Since $b \ll r$, we have $r' \approx r(1 - \frac{b}{r}\sin\theta\cos\phi')$, so $\frac{1}{r'} \approx \frac{1}{r}(1 + \frac{b}{r}\sin\theta\cos\phi')$. As seen in the figure, the x components from symmetrically placed points on either side of the x axis will cancel. Thus, $\vec{A}$ has only a y component. Here, we assume that $b \ll \lambda$. In this case, we have the approximate relation

$$\cos[\omega(t - r'/c)] \approx \cos[\omega(t - r/c)] - b\frac{\omega}{c}\sin\theta\cos\phi'\sin[\omega(t - r/c)]$$

Dropping the second-order terms, one obtains the approximate vector potential:

$$\vec{A}(r,\theta,t) = \frac{\mu_0 m_0}{4\pi r}\sin\theta\left\{\frac{1}{r}\cos[\omega(t - r/c)] - \frac{\omega}{c}\sin[\omega(t - r/c)]\right\}\hat{\phi}'$$

In the **far-field region** ($r \gg \lambda$), the above equation takes the form

$$\vec{A}(r,\theta,t) = -\frac{\mu_0 m_0 \omega}{4\pi c r}\sin\theta\sin[\omega(t - r/c)]\hat{\phi}'$$

Electric Dipole versus Magnetic Dipole

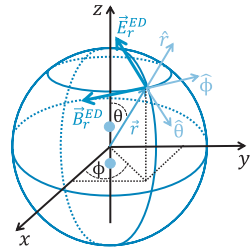
Here we compare electric fields with magnetic fields as well as the time-averaged radiated power associated with electric and magnetic dipole radiation in the **far-field region** ($r \gg \lambda$). For an **electric dipole** (ED) and a **magnetic dipole** (MD), the electric and magnetic fields are expressed as

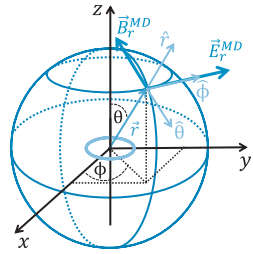
$$\vec{E}_r^{ED}(\vec{r},t) \approx -\frac{\mu_0 p \omega^2}{4\pi r}\sin\theta\cos\left[\omega\left(t-\frac{r}{c}\right)\right]\hat{\theta}$$

$$\vec{B}_r^{ED}(\vec{r},t) \approx -\frac{\mu_0 p \omega^2}{4\pi rc}\sin\theta\cos\left[\omega\left(t-\frac{r}{c}\right)\right]\hat{\phi}$$

$$\vec{E}_r^{MD}(\vec{r},t) \approx +\frac{\mu_0 m \omega^2}{4\pi rc}\sin\theta\cos\left[\omega\left(t-\frac{r}{c}\right)\right]\hat{\phi}$$

$$\vec{B}_r^{MD}(\vec{r},t) \approx -\frac{\mu_0 m \omega^2}{4\pi rc^2}\sin\theta\cos\left[\omega\left(t-\frac{r}{c}\right)\right]\hat{\theta}$$





The $\vec{E}$ and $\vec{B}$ vectors for the MD are rotated 90 deg compared to the case of the ED.

The time-averaged electromagnetic radiated power associated with an oscillating electric or magnetic multipole can be estimated as $\langle P(\vec{r},t)\rangle = \int_S \langle \vec{S}(\vec{r},t)\rangle \cdot d\vec{a}_s$, where $d\vec{a}_s = r^2 \sin\theta d\theta d\phi \hat{r}$. Poynting's vector $\vec{S}(\vec{r},t) = \mu_0^{-1}\vec{E}_r(\vec{r},) \times \vec{B}_r(\vec{r},t)$ describes the electromagnetic energy radiated by an oscillating dipole in the far-field region. Thus, for the ED and MD we have, respectively,

$$\langle P^{ED}(\vec{r},t)\rangle \approx \frac{\mu_0 p^2 \omega^4}{12\pi c}, \text{ and } \langle P^{MD}(\vec{r},t)\rangle \approx \frac{\mu_0 m^2 \omega^4}{12\pi c^3}$$

Here, we assume that $d = \pi b$ and that the MD is formed by rotation of a point charge q_0 at a constant frequency ω; i.e., $I_0 = q_0\omega$. In this case,

$$\frac{\langle P^{MD}(\vec{r},t)\rangle}{\langle P^{ED}(\vec{r},t)\rangle} = \frac{\omega b}{c} = \frac{2}{\lambda}\pi b \ll 1$$

Indeed, in the far-field region, $d = \pi b \ll \lambda \ll r$.

Quantization of the Electromagnetic Field

If many photons are present, an electromagnetic field can be described as a classical system. If the number of photons is small, an EM field cannot be considered as continuous. In this case, the EM field is considered as a **quantum object**. We will assume that the EM field is in vacuum (source free) and is enclosed in a finite cubic box of volume $V = L^3$. Its vector potential $\vec{A}$ is chosen such that $\nabla \cdot \vec{A} = 0$ (the **Coulomb gauge**). $\vec{A}$ can be decomposed into a Fourier series as

$$\vec{A}(\vec{r},t) = \sum_{\vec{k}} \sum_{\alpha=L,R} \left[\hat{e}_\alpha(\vec{k}) a_{k,\alpha}(t) e^{i\vec{k}\cdot\vec{r}} + c.c. \right]$$

where $c.c.$ is the complex conjugate term. The sum over $\vec{k}$ includes wave vectors in all directions. The components of vector $\vec{k}$ are $k_{x,y,z} = \frac{2\pi}{L} n_{x,y,z}$, $n_{x,y,z} = 0, \pm 1, \pm 2, \ldots$. Here, $\hat{e}_\alpha$ are unit polarization vectors for the left- (L) and right- (R) circularly polarized waves. The coefficients $a_{k,\alpha}(t)$ define the vector potential. Substituting $\vec{A}$ (presented as a Fourier series) into the wave equation for $\vec{A}$, one can find that $a_{k,\alpha}(t) = a_{k,\alpha} e^{-i\omega_k t}$, where $\omega_k = c|\vec{k}|$ is the frequency of the mode with wavenumber k. The electric field $\vec{E}$ and magnetic field $\vec{B}$ are expressed as

$$\vec{E}(\vec{r},t) = i \sum_{\vec{k}} \sum_{\alpha=L,R} \omega_k \left[\hat{e}_\alpha(\vec{k}) a_{k,\alpha}(t) e^{i\vec{k}\cdot\vec{r}} - c.c. \right]$$

$$\vec{B}(\vec{r},t) = i \sum_{\vec{k}} \sum_{\alpha=L,R} \left[(\vec{k} \times \hat{e}_\alpha(\vec{k})) a_{k,\alpha}(t) e^{i\vec{k}\cdot\vec{r}} - c.c. \right]$$

Each mode with frequency ω_k can be considered as a **quantum harmonic oscillator**. Considering the periodical boundary conditions for V, one can replace $a_{k,\alpha}$ with the operator $\hat{a}_{k,\alpha}$ as $a_{k,\alpha} \rightarrow \sqrt{\frac{\hbar}{2\omega_k \varepsilon_0 V}}\, \hat{a}_{k,\alpha}$. The operators $\hat{a}_{k,\alpha}$ must obey the commutation relations:

$$\left[\hat{a}^m_{k,\alpha}, \hat{a}^{n+}_{k,\alpha} \right] = \delta_{mn}, \left[\hat{a}^m_{k,\alpha}, \hat{a}^n_{k,\alpha} \right] = 0, \text{ and } \left[\hat{a}^{m+}_{k,\alpha}, \hat{a}^{n+}_{k,\alpha} \right] = 0$$

Quantization of the Electromagnetic Field (cont.)

In this case, the **quantized** (**operator**) **vector potential** and the **electric** and **magnetic fields** are written as

$$\vec{A}(\vec{r},t) = \sum_{\vec{k}} \sum_{\alpha=L,R} \sqrt{\frac{\hbar}{2\omega_k \varepsilon_0 V}} \left[\hat{e}_\alpha(\vec{k}) \hat{a}_{k,\alpha} e^{i\vec{k}_n \cdot \vec{r}} + c.c. \right]$$

$$\vec{E}(\vec{r},t) = i \sum_{\vec{k}} \sum_{\alpha=L,R} \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \left[\hat{e}_\alpha(\vec{k}) \hat{a}_{k,\alpha} e^{i\vec{k}_n \cdot \vec{r}} - c.c. \right]$$

$$\vec{B}(\vec{r},t) = i \sum_{\vec{k}} \sum_{\alpha=L,R} \sqrt{\frac{\hbar}{2\omega_k \varepsilon_0 V}} \left[(\vec{k} \times \hat{e}_\alpha(\vec{k})) \hat{a}_{k,\alpha} e^{i\vec{k} \cdot \vec{r}} - c.c. \right]$$

where $\vec{k}_n = \frac{2\pi}{L}(n_x\hat{x} + n_y\hat{y} + n_z\hat{z})$, and $\hat{e}_\alpha(\vec{k}) \cdot \vec{k}_n = 0$.

$E_0 = \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}$ is the **electric field per photon**

The classical Hamiltonian can be presented as

$$H = \frac{1}{2}\varepsilon_0 \iiint (|\vec{E}(\vec{r},t)|^2 + c^2 |\vec{B}(\vec{r},t)|^2) d^3\vec{r}$$

Substituting the quantized electric and magnetic fields in this relation, one obtains the **Hamilton operator of the EM field**:

$$\hat{H} = \sum_{\vec{k}} \sum_{\alpha=L,R} \hbar\omega_k \left(\hat{a}^\dagger_{k,\alpha} \hat{a}_{k,\alpha} + \frac{1}{2} \right) = \sum_{\vec{k}} \sum_{\alpha=L,R} \hbar\omega_k \left(\hat{n}_{k,\alpha} + \frac{1}{2} \right)$$

where $\hat{n}_{k,\alpha} = \hat{a}^\dagger_{k,\alpha} \hat{a}_{k,\alpha}$ is the **number operator**. Its eigenstates $|n_{k,\alpha}\rangle$,

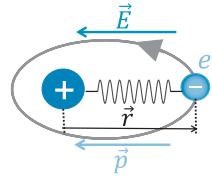
$$\hat{n}_{k,\alpha} |n_{k,\alpha}\rangle = n_{k,\alpha} |n_{k,\alpha}\rangle$$

are known as **number states** or **Fock states**. $\hat{a}_{k,\alpha}$ and $\hat{a}^\dagger_{k,\alpha}$ are **annihilation** and **creation operators**, respectively, and have the following properties:

$$\hat{a}_{k,\alpha} |n_{k,\alpha}\rangle = \sqrt{n_{k,\alpha}} |n_{k,\alpha} - 1\rangle, \quad \hat{a}^\dagger_{k,\alpha} |n_{k,\alpha}\rangle = \sqrt{n_{k,\alpha} + 1} |n_{k,\alpha} + 1\rangle$$

Polarization of a Dielectric Medium

Consider an **isotropic dielectric**, i.e., a material that contains no free electrons. Its positive charges are associated with the nuclei, and its negative charges are associated with the electrons bound to nuclei. The applied electric field results in a slight shift of the electron relative to its nucleus in atoms and produces an induced dipole $\vec{p} = e\vec{r}$, where e is the displaced electronic charge, and $\vec{r}$ is the vector that locates the negative charge center relative to the positive one. The **polarization of the medium**,



$$\vec{P} = Ne\vec{r}$$

is the collective dipole moment per unit volume. Here, N is the number of dipoles per unit volume. In a simple model, electrons are coupled by springs to nuclei and behave according to Hooke's law. Applying Newton's second law to the electron in the atom, we have Newton's equation of motion:

$$m_e \frac{d^2\vec{r}}{dt^2} + m_e\gamma\frac{d\vec{r}}{dt} + k_{sp}\vec{r} = e\vec{E}$$

where k_{sp} is the spring constant, γ is a friction constant, and $\vec{E}$ is the applied electric field. In a harmonic applied field, $\vec{E} = \vec{E}_0 e^{-i\omega t}$, the oscillator response is $\vec{r} = \vec{r}_0 e^{-i\omega t}$. The contribution to the total electric field at the position of a given dipole (due to all the other dipoles in the medium) is $\vec{P}/3\varepsilon_0$. This must be added to the applied field $\vec{E}$. In this case, it is evident from the equation of motion that the polarization of a dielectric medium is

$$\vec{P} = \left(\frac{Ne^2}{-m_e\omega^2 - im_e\omega\gamma + k_{sp}}\right)\left(\vec{E} + \frac{\vec{P}}{3\varepsilon_0}\right) \Rightarrow$$

$$\boxed{\vec{P} = \left(\frac{Ne^2/m_e}{\omega_0^2 - \omega^2 - i\omega\gamma}\right)\vec{E}}$$

where $\omega_0^2 = \frac{k_{sp}}{m_e} - \frac{Ne^2}{3m_e\varepsilon_0}$ is the **resonance frequency**.

- If $\omega \ll \omega_0$, $\vec{P}$ and $\vec{E}$ have the same sign, and the dipoles oscillate in phase with the field.
- If $\omega \gg \omega_0$, $\vec{P}$ and $\vec{E}$ have a phase difference of π.
- If $\omega \approx \omega_0$, a $\pi/2$ phase shift takes place between $\vec{P}$ and $\vec{E}$.

Light Propagation in a Dielectric

Maxwell defined the **displacement vectors** as

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \quad \text{and} \quad \vec{B} = \mu_0 \vec{H} + \vec{M}$$

Here $\vec{M}$ is the magnetization (the magnetic dipole moment per unit volume) of a medium. In a **dielectric**, the interaction of matter with the magnetic field of light is usually ignored, since it is several orders of magnitude weaker compared to the interaction with the electric field of light; i.e., $\vec{M} = 0$.

In dielectrics, also, the charge density $\rho = 0$ and the current $\vec{J} = 0$. Consider Maxwell's equations. Taking the curl of both sides of $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$ and the time derivative of $\nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}$, where $\vec{H} = \mu_0^{-1} \vec{B}$, one can obtain the equation

$$c^2 \nabla^2 \vec{E} = \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{1}{\varepsilon_0} \frac{\partial^2 \vec{P}}{\partial t^2}$$

Substituting the relation for the polarization of a dielectric medium $\vec{P}$, we have the equation

$$c^2 \nabla^2 \vec{E} = \left[1 + \frac{Ne^2}{m_e \varepsilon_0 (\omega_0^2 - \omega^2 - i\omega\gamma)} \right] \frac{\partial^2 \vec{E}}{\partial t^2}$$

For a harmonic wave, $\vec{E} = \vec{E}_0 e^{-i(kz - \omega t)}$, and from this equation, one can obtain the relation for the **propagation constant**, $k = k_r + ik_i$, which is written as

$$k^2 = \frac{\omega^2}{c^2} \left[1 + \frac{Ne^2}{m_e \varepsilon_0 (\omega_0^2 - \omega^2 - i\omega\gamma)} \right]$$

In this case, the relation for the harmonic has the form $\vec{E} = \vec{E}_0 e^{-k_i z} e^{-i(k_r z - \omega t)}$, where k_i describes the **amplitude attenuation** of the wave. The **energy flux density** is

$$I(z) = I_0 e^{-\alpha z}$$

where $\alpha = 2k_i$ is the **absorption coefficient**.

Normal and Anomalous Dispersion

The propagation constant k of a wave traveling with phase velocity v in a medium with refractive index n is

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{v} = \left(\frac{\omega}{c}\right)n, \quad \text{where } \boxed{n = n_r + in_i}$$

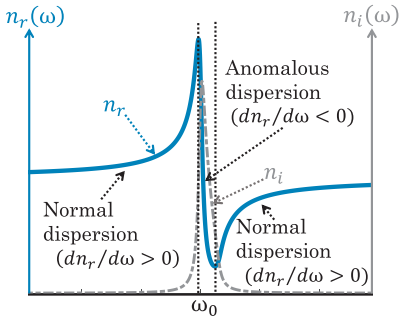
That is, $n^2 = (n_r + in_i)^2 = (n_r^2 - n_i^2) + i2n_r n_i = (\frac{c}{\omega}k)^2$. Using these relations, and accounting for the dependence of the propagation constant from the frequency of the light, one can obtain the relations

$$\boxed{n_r^2 - n_i^2 = 1 + \frac{Ne^2}{m_e\varepsilon_0}\left[\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}\right]}$$

and

$$\boxed{2n_r n_i = \frac{Ne^2}{m_e\varepsilon_0}\left[\frac{\omega\gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}\right]}$$

From these relations, we can obtain the values of n_r and n_i as functions of the frequency ω. In any region where n_r increases with ω, or $dn_r/d\omega > 0$, **normal dispersion** occurs. The narrow region where n_r decreases with ω, or $dn_r/d\omega < 0$, is called the region of **anomalous dispersion**. In this region, the absorption is very high.



Here we assume that $\gamma\omega \ll (\omega_0^2 - \omega^2)$ and $\omega \ll \omega_0$. In this case, the refractive index takes the following form (the **Cauchy dispersion equation**):

$$\boxed{n^2 \approx 1 + \frac{Ne^2}{m_e\varepsilon_0}\left(\frac{1}{\omega_0^2 - \omega^2}\right) \approx 1 + \frac{Ne^2}{m_e\varepsilon_0\omega_0^2}\left(1 + \frac{\omega^2}{\omega_0^2} + \frac{\omega^4}{\omega_0^4} + \ldots\right), \text{ or}}$$

$$\boxed{n \approx A + \frac{B}{\lambda^2} + \frac{C}{\lambda^3} + \ldots, \text{ where } A, B, C \text{ are constants.}}$$

Light Propagation in a Metal

In **metals**, in addition to bound electrons, there are free electrons. The response of the **free electrons** dominates the optical properties of the metal medium. The equation of motion for these free electrons with $k_{sp} = 0$ is

$$m_e \frac{d^2\vec{r}}{dt^2} + m_e\gamma\frac{d\vec{r}}{dt} = e\vec{E}$$

We introduce the **conduction current density** as $\vec{J} = Ne\frac{d\vec{r}}{dt}$. The equation of motion in terms of $\vec{J}$ is

$$\frac{d\vec{J}}{dt} + \gamma\vec{J} = \left(\frac{Ne^2}{m_e}\right)\vec{E}$$

If the applied field is a harmonic wave $\vec{E} = \vec{E}_0 e^{-i\omega t}$, the expected current density changes as $\vec{J} = \vec{J}_0 e^{-i\omega t}$. From the equation for the conduction current density $\vec{J}$, we have

$$\vec{J} = \left(\frac{\sigma}{1 - i\omega/\gamma}\right)\vec{E}, \text{ where } \boxed{\sigma = \frac{Ne^2}{m_e\gamma}} \text{ is the } \textbf{conductivity}.$$

Although free charges exist in the metal, the internal free-charge volume density $\rho = 0$. As in the case of the dielectric medium, we take the curl of both sides of the equation $\vec{\nabla} \times \vec{E} = -\frac{\partial\vec{B}}{\partial t}$ and the time derivative of the equation $\vec{\nabla} \times \vec{H} = \vec{j} + \frac{\partial\vec{D}}{\partial t}$. We now have the equation

$$c^2\nabla^2\vec{E} = \frac{\partial^2\vec{E}}{\partial t^2} + \frac{1}{\varepsilon_0}\frac{\partial\vec{J}}{\partial t}$$

Taking into account the relation for $\vec{J}$ and the relation for a harmonic wave $\vec{E} = \vec{E}_0 e^{-i(kz-\omega t)}$, one can obtain the relation for the **propagation constant**:

$$\boxed{k^2 = \frac{\omega^2}{c^2} + i\left(\frac{\sigma\omega\mu_0}{1 - i\omega/\gamma}\right)}$$

If ω is small, $k^2 \approx i\sigma\omega\mu_0$, and

$$k = k_r + ik_i = (1 + i)\left(\frac{\sigma\omega\mu_0}{2}\right)^{1/2}$$

where $\boxed{\delta = \frac{1}{k_i} = \left(\frac{2}{\sigma\omega\mu_0}\right)^{1/2}}$ is the **skin depth**.

Polaritons

Light propagating in matter is a mixture of an EM wave and a polarization wave. Like EM and polarization waves, mixed waves can be quantized. Quasi-particles of light in matter are known as **polaritons**, a term that combines polarization and photons. Polaritons were originally considered in crystalline solids by J. J. Hopfield and D. G. Thomas in 1963. Later, this approach was developed for noncrystalline solids, liquids, and gases. Polarization waves can include motions of electron–hole pair excitations in semiconductors, collective motions of electron clouds with respect to the nuclei, and so on. There are three types of polaritons: **phonon polaritons**, **exciton polaritons**, and **plasmon polaritons**.

In the quantum mechanical approach, the Hamiltonian of a system with mixed waves is written as

$$\hat{H} = \sum_k \hbar\omega_k \hat{a}_k^+ \hat{a}_k + \sum_{k'} E(\vec{k}')\hat{B}_{k'}^+ \hat{B}_{k'} + i\hbar \sum_k g_k(\hat{B}_k^+ \hat{a}_k + h.c.)$$

where *h.c.* is the Hermitian conjugate, $E(\vec{k}')$ is the quantum energy, and $\hat{a}_k^+ \hat{a}_k$ and $\hat{B}_k^+ \hat{B}_k$ are the number operators of the photons and quasi-particles in the medium, respectively. The third term in the Hamiltonian describes the interaction of the photons and the quasi-particles, e.g., the annihilation of a photon $\hat{a}_k$ and the creation of another quasi-particle (e.g., a phonon) $\hat{B}_k^+$, or vice versa. g_k is the transition probability. This Hamiltonian can be diagonalized according to the Bogoliubov transformation:

$$\boxed{\hat{H} = \sum_k E_k \hat{P}_k^+ \hat{P}_k,} \quad \text{where} \quad \hat{P}_k = \upsilon_k \hat{a}_k + u_k \hat{B}_k$$

where υ_k and u_k are suitable coefficients. $\hat{P}_k$ and $\hat{P}_k^+$ are the annihilation and creation operators, respectively, for the quanta of the polaritons with energy E_k.

In the classical approach, the wave vector in the medium $\vec{k}$ is associated with the wave vector of light in vacuum $\vec{k}_0$ by the refractive index $n(\omega) = \varepsilon(\omega)^{1/2}$ as $|\vec{k}|^2 = n^2(\omega)|\vec{k}_0|^2$, $|\vec{k}_0| = \frac{\omega}{c}$. From this relation, we can obtain

$$\boxed{\frac{c^2k^2}{\omega^2} = \varepsilon(\omega) \quad (\text{the } \textbf{polariton dispersion equation}).}$$

Dielectric Function

Assume a linear relationship between the applied electric field $\vec{E}$ and the polarization of the medium $\vec{P}$; i.e., $\vec{P} = \varepsilon_0 \chi \vec{E}$ or $\vec{D} = \varepsilon_0(1+\chi)\vec{E} = \varepsilon_0 \varepsilon \vec{E}$. Here, $\varepsilon = 1 + \chi$ is the **dielectric function**, and χ is the susceptibility of the medium. Both quantities (ε and χ) depend on the frequency ω and wave vector $\vec{k}$. ε is associated with the refractive index as $\varepsilon(\omega, \vec{k}) = n^2(\omega, \vec{k})$.

In most cases, a medium contains not only one type of oscillation and one resonance frequency ω_0, but many, including phonons, excitons, plasmons, etc. In linear optics, one can simply sum over all resonances. In this case, $\varepsilon(\omega) = 1 + \sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 - i\omega\gamma_j}$, where f_j is the oscillator strength.

This relation is known as the **Helmholtz–Ketteler formula** or the **Kramers–Heisenberg dielectric function**. Near a resonance $\omega_{0j'}$, we can neglect the contributions from all lower ($\omega_{0j} \ll \omega_{0j'}$) resonances. The contributions from all higher ($\omega_{0j} \gg \omega_{0j'}$) resonances can be summarized in a background dielectric constant ε_∞. In this case, the **dielectric function** is written as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \frac{f_{j'}}{\omega_{0j'}^2 - \omega^2 - i\omega\gamma_{j'}}$$

If ε is near the optical phonon resonances ω_{LO} and ω_{TO},

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\gamma}\right) \Rightarrow \textbf{phonon polaritons}$$

If ε is for a metal with plasma frequency $\omega_p = \mu_0 c^2 \gamma \sigma$,

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \Rightarrow \textbf{plasmon polaritons}$$

If ε is for a semiconductor with exciton mass $M = m_e + m_h$, where m_e and m_h are electron and hole masses, respectively,

$$\varepsilon(\omega, k) = \varepsilon_\infty \left(1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 + \beta k^2 - i\omega\gamma}\right) \Rightarrow \textbf{exciton polaritons}$$

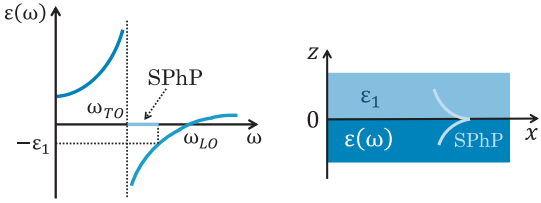
where $\beta = \hbar\omega_{TO}/M$.

Surface Polaritons

Surface polaritons are EM waves propagating at the interface of two media having dielectric permittivities of differing signs. By way of example, consider **surface phonon polaritons** (SPhPs), which are EM surface modes formed by the strong coupling of light and optical phonons in polar crystals, and are generally excited using infrared (IR) or terahertz (THz) radiation.

A surface polariton can exist only as a **transverse magnetic** (TM) wave, with its magnetic field parallel to the interface (H_y), while the electric field has both components perpendicular to the interface (E_z) and along the propagation direction (E_x). From Maxwell's equations for vanishing charges and currents, and for nonmagnetic media ($\mu = 1$), one can obtain the equation for the electric field:

$$\frac{\partial^2 E_x}{\partial z^2} + \varepsilon \frac{\omega^2}{c^2} E_x - \frac{\partial^2 E_z}{\partial x \partial z} = 0$$



For simplicity, we consider a medium with $\varepsilon_2(\omega)$ without loss ($\gamma = 0$). Now we can present the electric field as

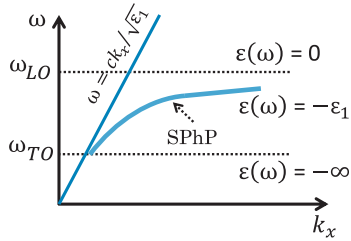
$$\vec{E} = \vec{E}^{(1)} e^{(ik_x x - k_z^{(1)} z)}, z > 0 \text{ and } \vec{E} = \vec{E}^{(2)} e^{(ik_x x + k_z^{(2)} z)}, z < 0$$

Substituting these relations into the equation for the electric field, and accounting for the boundary conditions at $z = 0$, $E_x^{(1)} = E_x^{(2)}$ and $\varepsilon_1 E_z^{(1)} = \varepsilon(\omega) E_z^{(2)}$, one obtains

$$\frac{\varepsilon(\omega)}{k_z^{(2)}} = -\frac{\varepsilon_1}{k_z^{(1)}} \Rightarrow$$

$$\boxed{k_x^2 = \frac{\omega^2}{c^2} \frac{\varepsilon_1 \varepsilon(\omega)}{\varepsilon_1 + \varepsilon(\omega)}}$$

(the **dispersion equation**).



Resonant Linear Susceptibility

As we know from the optical Bloch equations, the ensemble average of the dipole momentum is $\langle\overline{\mu}\rangle = Tr(\rho\hat{\mu}) = \mu_d(\rho_{12} + \rho_{21}) = 2\mu_d[\mathrm{Re}(\beta_{21})\cos\omega t + \mathrm{Im}(\beta_{21})\sin\omega t]$. Consider what happens in the steady state, i.e., when the system has settled, such that $d(\rho_{11} - \rho_{22})/dt = 0$ and $d\beta_{21}/dt = 0$. In this case, using the **optical Bloch equations**, we have

$$\rho_{11} - \rho_{22} = (\rho_{11} - \rho_{22})_0 \frac{1 + (\omega - \omega_0)^2 T_2^2}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\mathrm{Re}(\beta_{21}) = \frac{\Omega T_2^2(\rho_{11} - \rho_{22})}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

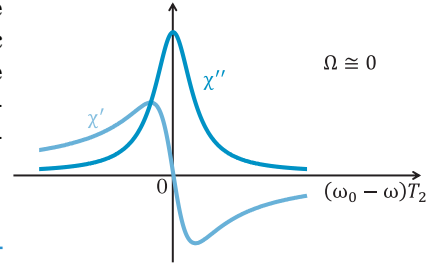
$$\mathrm{Im}(\beta_{21}) = \frac{\Omega T_2(\omega_0 - \omega)(\rho_{11} - \rho_{22})}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

In electromagnetism, the polarization $P = \varepsilon_0\chi E = \varepsilon_0 E_0(\chi'\cos\omega t + \chi''\sin\omega t)$, where $\chi = \chi' + i\chi''$ is the **susceptibility**, and E is an oscillating electric field. In the quantum mechanical approach, the polarization is the dipole moment per unit volume $P = N_T\langle\overline{\mu}\rangle$, where N_T is the dipole density, $\langle\overline{\mu}\rangle = Tr(\rho\hat{\mu})$ is the expectation value of the dipole, $\hat{\mu}$ is the dipole operator, and ρ is the density matrix. Thus, we can write

$$\chi'(\omega) = \frac{\Delta N_0 T_2 \mu_d^2}{\varepsilon_0\hbar} \frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\chi''(\omega) = \frac{\Delta N_0 T_2 \mu_d^2}{\varepsilon_0\hbar} \frac{1}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

where $\Omega = \mu_d E_0/2\hbar$, the population difference $\Delta N = N_T(\rho_{11} - \rho_{22})$, and $\Delta N_0 = N_T(\rho_{11} - \rho_{22})_0$ in the absence of the optical field. If the amplitude of the electric field is small, $\Omega \cong 0$, we have a refraction variation line χ'' and a Lorentzian absorption line χ'.



$$4\Omega^2 T_2 T_1 = I/I_s,$$

where I_s is the **saturation intensity**. At resonance ($\omega = \omega_0$), we have $\chi''(\omega) \propto 1/(1 + I/I_s)$.

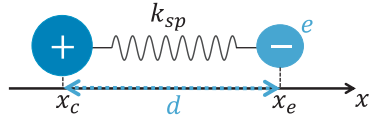
Anharmonic Oscillator

The first successful experiment on second-harmonic generation, made by Peter Franken and his colleagues in 1961, can be considered as the birth of nonlinear optics. One needs to apply a beam intensity of ~ 2.5 kW/cm^2 to induce a nonlinear response in a medium, and a laser beam is needed to reach this target.

If the field is sufficiently intense and its frequency is sufficiently far from any medium resonances, the polarization $\vec{P}$ as a function of the electric field $\vec{E}$ can be expanded into a power series of the electric field. The simplest model of interaction between light and matter is the classical oscillator consisting of an electron that is mutually interacting with a positively charged core through attractive Coulomb forces. If the wavelength of the field $\lambda \gg d = (x_e - x_c)$, one can neglect any spatial variations of the fields over the spatial extent of the oscillator system. The restoring nonlinear central force is modeled by a mechanical spring force with a **spring constant** given as

$$k_{sp} = k_{sp}^{(0)} - 2k_{sp}^{(1)}(x_e - x_c)$$

Newton's equations of motion for the electron m_e and core m_c, respectively, are



$$m_e \frac{\partial^2 x_e}{\partial t^2} = eE(t) - k_{sp}^{(0)}(x_e - x_c) + k_{sp}^{(1)}(x_e - x_c)^2$$

$$m_c \frac{\partial^2 x_c}{\partial t^2} = -eE(t) + k_{sp}^{(0)}(x_e - x_c) - k_{sp}^{(1)}(x_e - x_c)^2$$

We introduce the reduced mass of the system as $m_r = m_e m_c/(m_e + m_c)$. In this case, the equation of motion for the value of the electric dipole moment $p = e(x_e - x_c)$ is

$$\frac{\partial^2 p}{\partial t^2} + \frac{k_{sp}^{(0)}}{m_r} p - \frac{k_{sp}^{(1)}}{e m_r} p^2 = \frac{e^2}{m_r} E(t)$$

We present the electric dipole moment of the **anharmonic oscillator** in terms of a perturbation series as $p(t) = p^{(0)}(t) + p^{(1)}(t) + p^{(2)}(t) + p^{(3)}(t) + \ldots$. Each term in the series is proportional to the value of the applied electrical field E as $p^{(n)}(t) \propto E^n(t)$, where $n = 0, 1, 2, \ldots$.

First-Order Classical Electric Susceptibility

Now we insert the electric dipole moment of the anharmonic oscillator (presented as a perturbation series) into the equation of motion for the value of the electric dipole moment. We have the following **system of equations**:

$$\frac{\partial^2 p^{(0)}}{\partial t^2} + \frac{k_{sp}^{(0)}}{m_r} p^{(0)} - \frac{k_{sp}^{(1)}}{e m_r} (p^{(0)})^2 = 0$$

$$\frac{\partial^2 p^{(1)}}{\partial t^2} + \frac{k_{sp}^{(0)}}{m_r} p^{(1)} - \frac{k_{sp}^{(1)}}{e m_r} 2 p^{(0)} p^{(1)} = \frac{e^2}{m_r} E(t)$$

$$\frac{\partial^2 p^{(2)}}{\partial t^2} + \frac{k_{sp}^{(0)}}{m_r} p^{(2)} - \frac{k_{sp}^{(1)}}{e m_r} [2 p^{(0)} p^{(2)} + (p^{(1)})^2] = 0$$

$$\frac{\partial^2 p^{(3)}}{\partial t^2} + \frac{k_{sp}^{(0)}}{m_r} p^{(3)} - \frac{k_{sp}^{(1)}}{e m_r} 2 [p^{(0)} p^{(3)} + p^{(1)} p^{(2)}] = 0$$

We will not consider molecular systems such as water, where a permanent static dipole moment is present. Consider a system starting from rest. We can set $p^{(0)}(t) = 0$ (not to be confused with the static polarization induced by the electric field). Inserting a time-harmonic electric field $E(t) = E_\omega \cos(\omega t)$ into the second equation of the system, we have

$$p^{(1)}(t) = \frac{(e^2/m_r)}{(k_{sp}^{(0)}/m_r - \omega^2)} E_\omega \cos(\omega t)$$

If a material contains N dipoles per unit volume, the first-order electric polarization density has the form

$$P^{(1)}(t) = P_\omega^{(1)} \cos(\omega t) = \varepsilon_0 \chi^{(1)}(\omega) E_\omega \cos(\omega t)$$

where the **first-order** (**linear**) **susceptibility** is

$$\chi^{(1)}(\omega) = \frac{N}{\varepsilon_0} \frac{(e^2/m_r)}{(\omega_0^2 - \omega^2)}$$

where

$\omega_0^2 = k_{sp}^{(0)}/m_r$ is the **resonance frequency**.

Second-Order Classical Electric Susceptibility

In the second-order case, we insert the relation for the first-order electric polarization density $p^{(1)}(t)$ in the third equation of the system of equations for the terms of a perturbation series of the electric dipole moment of an anharmonic oscillator. Solving this equation, we have the relation for the second-order perturbation term:

$$p^{(2)}(t) = \frac{k_{sp}^{(1)} e^3}{2m_r^3} \frac{E_\omega^2}{\omega_0^2(\omega_0^2-\omega^2)^2} + \frac{k_{sp}^{(1)} e^3}{2m_r^3} \frac{E_\omega^2}{(\omega_0^2-4\omega^2)(\omega_0^2-\omega^2)^2} \cos(2\omega t)$$

If a material contains N dipoles per unit volume, the second-order electric polarization density has the form

$$P^{(2)}(t) = P_0^{(2)} + P_{2\omega}^{(2)} \cos(2\omega t) = \frac{\varepsilon_0}{2}\chi^{(2)}(0;\omega,-\omega)E_\omega E_\omega + \frac{\varepsilon_0}{2}\chi^{(2)}(2\omega;\omega,\omega)E_\omega E_\omega \cos(2\omega t)$$

Here the first term is the zero-frequency polarization component, known as **optical rectification** or **DC electric polarization**. The second term is the second-harmonic polarization. The **second-order** (**quadratic**) **electric susceptibility** is written as

$$\chi^{(2)}(0;\omega,-\omega) = \frac{N}{\varepsilon_0}\frac{k_{sp}^{(1)} e^3}{m_r^3}\frac{E_\omega^2}{\omega_0^2(\omega_0^2-\omega^2)^2}$$

$$\chi^{(2)}(2\omega;\omega,\omega) = \frac{N}{\varepsilon_0}\frac{k_{sp}^{(1)} e^3}{m_r^3}\frac{E_\omega^2}{(\omega_0^2-4\omega^2)(\omega_0^2-\omega^2)^2}$$

In a similar way, using the fourth equation of the system of equations for the terms of a perturbation series of the electric dipole moment $p(t)$, the **third-order electric susceptibility** $\chi^{(3)}$ can be obtained. All values of $\chi^{(n)}$ are related to the microscopic structure of the medium. They can be more properly evaluated using the quantum-mechanical approach.

Time-Dependent Perturbation Theory

Time-dependent perturbation theory is a technique that can be used to investigate the time response of a quantum mechanical system to changes in its environment. The technique can be used, for example, to understand how quantum mechanical systems respond to light. Assume that $\hat{H}_p(t)$ is the operator of time-dependent perturbation to $\hat{H}_0$, which is the Hamiltonian of an unperturbed system. In this case, the total Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{H}_p(t)$. It must satisfy the time-dependent Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$. If $|\varphi_n\rangle$ and E_n are the energy eigenfunctions and eigenvalues, respectively, of the time-independent Schrödinger equation $\hat{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle$, we can expand this to $|\Psi\rangle = \sum_n a_n(t)e^{-iE_nt/\hbar}|\varphi_n\rangle$. Substituting this expansion into the time-dependent Schrödinger equation, and accounting for the time-independent Schrödinger equation, and multiplying by $\langle\phi_n|$ on both sides, one obtains the relation

$$i\hbar\frac{\partial}{\partial t}a_q(t)e^{-iE_qt/\hbar} = \sum_n a_n(t)e^{-iE_nt/\hbar}\langle\varphi_q|\hat{H}_p(t)|\varphi_n\rangle$$

We assume that the coefficients $a_n(t)$ can be presented as a power series $a_n(t) \cong a_n^{(0)}(t) + \gamma a_n^{(1)}(t) + \gamma^2 a_n^{(2)}(t) + \ldots$. Equating powers of γ on both sides of the equation, we obtain $\frac{\partial}{\partial t}a_q^{(0)}(t) = 0$; i.e., $a_q^{(0)}$ are constants that describe the starting state at $t = 0$. For the **first-order term**, we have

$$\frac{\partial}{\partial t}a_q^{(1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(0)}e^{i\omega_{qn}t}\langle\varphi_q|\hat{H}_p(t)|\varphi_n\rangle, \text{where } \omega_{qn} = \frac{(E_q - E_n)}{\hbar}$$

As can be seen from this equation, if we know the starting state $a_q^{(0)}$, the perturbing potential, and the unperturbed eigenvalues and eigenfunctions, we can calculate $a_q^{(1)}(t)$. Equating powers of higher orders, one obtains the equations that allow us to calculate **higher-order corrections**:

$$\frac{\partial}{\partial t}a_q^{(p+1)}(t) = \frac{1}{i\hbar}\sum_n a_n^{(p)}e^{i\omega_q t}\langle\varphi_q|\hat{H}_p(t)|\varphi_n\rangle$$

Perturbative Corrections in the Electric Field

Nonlinear optics is an excellent example of the application of high-order time-dependent perturbation theory. Here we calculate up to third-order perturbative corrections for a nonlinear system. The nonlinear optical effects involve electromagnetic fields with different frequencies ω_s. The total field can be presented as

$$E(t) = \sum_s E(\omega_s) e^{-i\omega_s t}, \text{ where } E(\omega_s) = E_{0\,s} e^{-i\delta_s}$$

A perturbing operator can be presented as

$$\hat{H}_p(t) = eE(t)z = ez \sum_s E(\omega_s) e^{-i\omega_s t}$$

We assume that the system is initially in the eigenstate m; i.e., $|\Phi^{(0)}\rangle = e^{-i\omega_m t}|\varphi_m\rangle$. In this case, the **first-order perturbation** is

$$\frac{\partial}{\partial t} a_q^{(1)}(t) = -\frac{\mu_{qm}}{i\hbar} \sum_s E(\omega_s) e^{i(\omega_{qm} - \omega_s)t}$$

where

$$\boxed{\mu_{qm} = -e\langle \varphi_q | \hat{z} | \varphi_m \rangle}$$

is the **electric dipole moment between states**. Integrating this equation, one can obtain

$$\boxed{a_q^{(1)}(t) = \frac{1}{\hbar} \sum_s \frac{\mu_{qm} E(\omega_s)}{(\omega_{qm} - \omega_s)} e^{i(\omega_{qm} - \omega_s)t}}$$

In a similar manner, using the equations for higher-order corrections $a_q^{(p+1)}(t)$, one can obtain the relations for the **second- and third-order corrections** as follows:

$$\boxed{\begin{aligned} a_q^{(2)}(t) &= \frac{1}{\hbar^2} \sum_q \sum_{s,u} \frac{\mu_{jq} E(\omega_u) \mu_{qm} E(\omega_s)}{(\omega_{jm} - \omega_s - \omega_u)(\omega_{qm} - \omega_s)} e^{i(\omega_{jm} - \omega_s - \omega_u)t} \\ a_q^{(3)}(t) &= \frac{1}{\hbar^3} \sum_{j,q} \sum_{s,u,v} \frac{\mu_{kj} E(\omega_v) \mu_{jq} E(\omega_u) \mu_{qm} E(\omega_s) e^{i(\omega_{km} - \omega_s - \omega_u - \omega_v)t}}{(\omega_{km} - \omega_s - \omega_u - \omega_v)(\omega_{jm} - \omega_s - \omega_u)(\omega_{qm} - \omega_s)} \end{aligned}}$$

Here j and q are applied to all states of the system, and s, u, v are applied to all frequencies of the electric fields.

Polarization Calculation

Almost all nonlinear effects can be described by second- and third-order perturbation theory, where the total state of the system can be presented as

$$|\Psi\rangle \cong |\Phi^{(0)}\rangle + |\Phi^{(1)}\rangle + |\Phi^{(2)}\rangle + |\Phi^{(3)}\rangle$$

Here $|\Phi^{(0)}\rangle$ is the unperturbed time-dependant state, and $|\Phi^{(1)}\rangle$, $|\Phi^{(2)}\rangle$ and $|\Phi^{(3)}\rangle$ are the first-, second-, and third-order correction terms, respectively. We can write the expectation value of the polarization using the operator of the dipole moment as

$$\begin{aligned}\langle P(t)\rangle &= \frac{1}{V}\langle\Psi|\hat{\mu}|\Psi\rangle \cong \frac{1}{V}\langle\Phi^{(0)} + \ldots + \Phi^{(3)}|\hat{\mu}|\Phi^{(0)} + \ldots + \Phi^{(3)}\rangle \\ &\cong \langle P^{(0)}(t)\rangle + \langle P^{(1)}(t)\rangle + \langle P^{(2)}(t)\rangle + \langle P^{(3)}(t)\rangle\end{aligned}$$

where

$$\langle P^{(0)}(t)\rangle = \frac{1}{V}\langle\Phi^{(0)}|\hat{\mu}|\Phi^{(0)}\rangle$$

is the **static polarization** of the material, which is present in several materials (e.g., ferroelectrics, which demonstrate a spontaneous polarization even in the absence of the applied field). $|\Phi^{(0)}\rangle = e^{-i\omega_m t}|\varphi_m\rangle$ is the **initial state** of the system.

The linear polarization, which gives the linear refractive index, is written as

$$\langle P^{(1)}(t)\rangle = \frac{1}{V}\left(\langle\Phi^{(0)}|\hat{\mu}|\Phi^{(1)}\rangle + \langle\Phi^{(1)}|\hat{\mu}|\Phi^{(0)}\rangle\right)$$

The **second-** and **third-order polarizations**, respectively, are

$$\begin{aligned}\langle P^{(2)}(t)\rangle &= \frac{1}{V}\left(\langle\Phi^{(0)}|\hat{\mu}|\Phi^{(2)}\rangle + \langle\Phi^{(2)}|\hat{\mu}|\Phi^{(0)}\rangle + \langle\Phi^{(1)}|\hat{\mu}|\Phi^{(1)}\rangle\right) \\ \langle P^{(3)}(t)\rangle &= \frac{1}{V}\left(\langle\Phi^{(0)}|\hat{\mu}|\Phi^{(3)}\rangle + \langle\Phi^{(3)}|\hat{\mu}|\Phi^{(0)}\rangle + \langle\Phi^{(1)}|\hat{\mu}|\Phi^{(2)}\rangle\right. \\ &\quad \left. + \langle\Phi^{(2)}|\hat{\mu}|\Phi^{(1)}\rangle\right)\end{aligned}$$

Linear and Nonlinear Susceptibilities

Time-dependent corrections can be presented as

$$|\Phi^{(j)}\rangle = \sum_n a_n^{(j)}(t)e^{-i\omega_n t/\hbar}|\varphi_n\rangle, \text{ where } j = 1, 2, 3$$

Using the relations for the $a_q^{(1)}(t)$ coefficient and the relation for the linear polarization $\langle P^{(1)}(t)\rangle$, we can obtain

$$\begin{aligned}\langle P^{(1)}(t)\rangle &= \frac{1}{V\hbar}\sum_q \sum_s \mu_{mq}\mu_{qm}\left(\frac{1}{(\omega_{qm}-\omega_s)}\right.\\ &\quad\left.+\frac{1}{(\omega_{qm}+\omega_s)}\right)E(\omega_s)e^{-i\omega_s t}\\ &= \varepsilon_0 \sum_s \chi^{(1)}(\omega_s;\omega_s)E(\omega_s)e^{-i\omega_s t}\end{aligned}$$

where

$$\chi^{(1)}(\omega_s;\omega_s) = \frac{1}{V\hbar\varepsilon_0}\sum_s \mu_{mq}\mu_{qm}\left(\frac{1}{(\omega_{qm}-\omega_s)}+\frac{1}{(\omega_{qm}+\omega_s)}\right)$$

The **linear susceptibility** $\chi^{(1)}$ gives rise to polarization at frequency ω_s in response to a field at the same frequency ω_s. In a similar manner, using the relations for the $a_q^{(2)}(t)$ coefficient and the relation for the second-order polarization $\langle P^{(2)}(t)\rangle$, we can obtain

$$\langle P^{(2)}(t)\rangle = \varepsilon_0 \sum_{s,u} \chi^{(2)}(\omega_u+\omega_s;\omega_u,\omega_s)E(\omega_u)E(\omega_s)e^{-i(\omega_u+\omega_s)t}$$

where the **second-order susceptibility** is written as

$$\begin{aligned}&\chi^{(2)}(\omega_u+\omega_s;\omega_u,\omega_s)\\ &\quad= \frac{1}{V\hbar^2\varepsilon_0}\sum_{j,q}\mu_{mj}\mu_{jq}\mu_{qm}\left(\frac{1}{(\omega_{jm}-\omega_u-\omega_s)(\omega_{qm}-\omega_s)}\right.\\ &\quad\left.+\frac{1}{(\omega_{jm}+\omega_u)(\omega_{qm}-\omega_s)}+\frac{1}{(\omega_{jm}+\omega_u+\omega_s)(\omega_{qm}+\omega_s)}\right)\end{aligned}$$

Here, the original field has two components at frequencies ω_u and ω_s. The second-order susceptibility $\chi^{(2)}$ is responsible for the strength of the generation process at the sum frequency $\omega_u + \omega_s$.

In a similar manner, using $a_q^{(3)}(t)$ and $\langle P^{(3)}(t)\rangle$, one can obtain the third-order susceptibility $\chi^{(3)}$.

Nonlinear Optical Effects

A major portion of nonlinear optical processes can be described by second- and third-order perturbation theory. Higher-order processes, which can also be described by higher-order perturbation theory, are usually quite weak.

❖ **Second-order effects** are generally the strongest effects. They can occur only in **noncentrosymmetric** crystals, i.e., in crystals that do not show inversion symmetry. These media include

- ✓ triclinic crystal systems
- ✓ monoclinic crystal systems
- ✓ orthorhombic crystal systems
- ✓ tetragonal crystal systems
- ✓ cubic crystal systems
- ✓ trigonal crystal systems
- ✓ hexagonal crystal systems

In these media, $\chi^{(2)} \neq 0$. The second-order effects are responsible for

- second harmonic generation
- the electro-optic effect, which is a linear variation of the refractive index with an applied static electric field (the Pockels effect)
- three-wave mixing phenomena

❖ **Third-order effects** can occur in both **centrosymmetric** and **noncentrosymmetric media**. For example, isotropic materials such as liquids, gases, and amorphous solids (e.g., glasses) do not show second-order phenomena ($\chi^{(2)} = 0$). Their lowest-order nonlinear effects are third-order effects ($\chi^{(3)} \neq 0$).

Third-order effects lead to

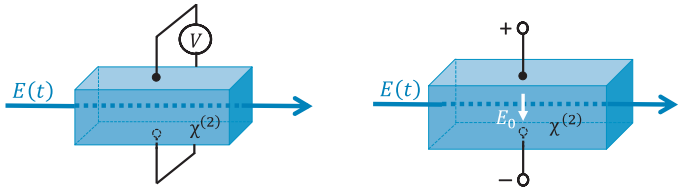
- an intensity-dependent refractive index, which changes in proportion to the square of the static electric field (the Kerr effect)
- third-harmonic generation
- four-wave mixing
- Raman and Brillouin scattering

The Linear Electro-Optic Effect

Consider nonlinear media in which nonlinearities of orders higher than the second are negligible. The polarization density of these media is $P = \varepsilon_0\chi^{(1)}E + P^{NL}$, where $P^{NL} \sim \varepsilon_0\chi^{(2)}E^2$. The response of these nonlinear media to a harmonic electric field $E(t) = E_\omega \cos(\omega t)$ is

$$P^{NL} = \frac{\varepsilon_0}{2}\chi^{(2)}(0;\omega,-\omega)E_\omega E_\omega + \frac{\varepsilon_0}{2}\chi^{(2)}(-2\omega;\omega,\omega)E_\omega E_\omega \cos(2\omega)$$

The first term in this relation is the optical rectification or the DC electric polarization, which creates a DC voltage across a nonlinear crystal.



We apply to the crystal, besides the harmonic electric field $E(t) = E_\omega \cos(\omega t)$, a steady electric field E_0. In this case, the **polarization density** will contain three components at the angular frequencies $0, \omega$, and 2ω:

$$P^{NL} = \varepsilon_0\chi^{(2)}\left[\tilde{P}_{NL}^{(0)} + \tilde{P}_{NL}^{(1)}\cos(\omega t) + \tilde{P}_{NL}^{(2)}\cos(2\omega t)\right]$$

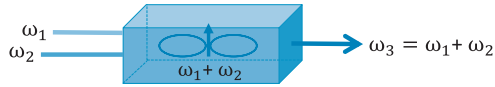
where $\tilde{P}_{NL}^{(0)} = E_0^2 + E_\omega^2/2$, $\tilde{P}_{NL}^{(1)} = 2E_0E_\omega$, and $\tilde{P}_{NL}^{(2)} = E_\omega^2/2$.

If $E_\omega \ll E_0$, the term $\tilde{P}_{NL}^{(2)}$ may be neglected. As a result, P^{NL} will be linearized. We present $P_{NL}^{(1)} = \varepsilon_0\chi^{(2)}\tilde{P}_{NL}^{(1)}$ as $P_{NL}^{(1)} = 2\varepsilon_0\chi^{(2)}E_0E_\omega = \varepsilon_0\Delta\chi E_\omega$, where $\Delta\chi = 2\chi^{(2)}E_0$ describes the change in the susceptibility, which is proportional to the applied steady electric field E_0. The corresponding change in the refractive index is $\Delta n = \chi^{(2)}E_0/n = -n^3rE_0/2$, where $r = -2\chi^{(2)}/n^4$ is the **Pockels coefficient**.

The refractive index of a medium can be modified by the applied electric field. This effect, known as the **linear electro-optic effect** or the **Pockels effect**, was first described by Fredrich Carl Pockels in 1893.

The Wave Equation for Nonlinear Media

Here we investigate how Maxwell's equations describe the generation of new field components and how the various frequency components of the field become coupled by nonlinear interaction. For definiteness, we consider the case of sum-frequency generation. The input fields have frequencies ω_1 and ω_2. As a result of **nonlinearity**, each atom radiates at the frequency $\omega_3 = \omega_1 + \omega_2$ in the form of a dipole radiation.



We assume here that a sample consists of N atoms. Each of these atoms oscillates with a phase determined by the phases of the incident fields. If this system of N dipoles (atoms) is phase-matched, the electric field radiated by the system will be N times larger than that of any atom. Using Maxwell's equations, one can obtain the wave equation for a nonmagnetic material that contains no free charges and no free currents as follows:

$$\nabla \times \nabla \times \vec{E} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E} = -\mu_0 \frac{\partial^2}{\partial t^2}\vec{P}$$

where $\vec{P} = \vec{P}^L + \vec{P}^{NL}$. Since the polarization vector includes the nonlinear part, this equation is called the **nonlinear wave equation**. We consider the electric field and polarization as the sums of their various frequency components:

$$\vec{E}(\vec{r},t) = \sum_n \left[\vec{E}_n(\vec{r})e^{-i\omega_n t} + c.c.\right]$$

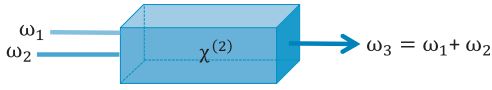
$$\vec{P}^{NL}(\vec{r},t) = \sum_n \left[\vec{P}_n^{NL}(\vec{r})e^{-i\omega_n t} + c.c.\right]$$

In this case, $n = 3$. The **nonlinear wave equation** is written as

$$\nabla \times \nabla \times \vec{E}_n - \frac{\omega_n^2}{c^2}\boldsymbol{\varepsilon}\vec{E}_n = \mu_0\omega_n^2\vec{P}_n^{NL}$$

$\boldsymbol{\varepsilon}$ is the linear dielectric tensor with $\varepsilon_{ij} = \delta_{ij} + \chi_{ij}^{(1)}$, where δ_{ij} is the Kronecker symbol.

Coupled-Wave Equations



Now we examine how nonlinear interactions can be described using the nonlinear wave equation. As an example, we consider sum-frequency generation.

If a nonlinear term is absent ($\vec{P}_n^{NL} = 0$) in the nonlinear wave equation, the solution to this equation is a plane wave $E_n(z,t) = A_n e^{i(k_n z - \omega_n t)} + c.c.$, where $n = 1, 2, 3$, and A_n is a constant. $k_n = \omega_n n(\omega_n)/c$, where $n(\omega_n)$ is the refractive index at the frequency ω_n. We assume that the nonlinear term $\vec{P}_n^{NL} \neq 0$, and it is not too large. In this case, we reason that the solution to the nonlinear wave equation saves its form; however, the A_n amplitude is a function of z. The nonlinear terms can be presented as $P_n^{NL} = P_n + c.c.$, where

$$P_3 = 4\varepsilon_0 d E_1 E_2, \quad P_1 = 4\varepsilon_0 d E_3 E_2^*, \quad \text{and} \quad P_2 = 4\varepsilon_0 d E_3 E_1^*$$

Here $d = \chi^{(2)}/2$ is known as the ***d* coefficient**. $E_i(z,t) = A_i(z)e^{i(k_i z - \omega_i t)} + c.c.$ is the applied electric field at the frequency ω_i, where $i = 1, 2$. Consider the **slowly varying-amplitude approximation** for the amplitudes $|\frac{d^2 A_n}{dz^2}| \ll |k_n \frac{dA_n}{dz}|$. Substituting the relations for electric fields E_n and polarizations P_n^{NL} into the nonlinear wave equation, and using an approximation $\nabla \times \nabla \times \vec{E} \cong -\nabla^2 \vec{E}$, which is valid for homogeneous media, one can obtain the system of equations known as the **coupled-wave equations**:

$$\frac{dA_1}{dz} = i\frac{2d\omega_1}{n(\omega_1)c} A_3 A_2^* e^{-i\Delta k z}$$

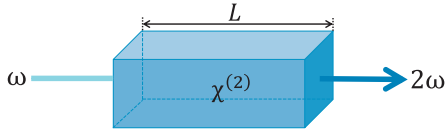
$$\frac{dA_2}{dz} = i\frac{2d\omega_2}{n(\omega_2)c} A_3 A_1^* e^{-i\Delta k z}$$

$$\frac{dA_3}{dz} = i\frac{2d\omega_3}{n(\omega_3)c} A_1 A_2 e^{i\Delta k z}$$

where $\Delta k = k_1 + k_2 - k_3$ are the **phase-matching conditions**. $\Delta k = 0$ is the **perfect phase matching**, and $L_c = 2/\Delta k$ is the **coherence length** of the interaction.

Second-Harmonic Generation

Second-harmonic generation, which, in 1961, was the first nonlinear process to be demonstrated, is a nonlinear effect in which two photons with the same frequency ω interact with a second-order nonlinear material. The result of this interaction is the generation of a new photon with twice the frequency 2ω of the initial photons.



The theory of second-harmonic generation is similar to the theory of sum-frequency generation. The **nonlinear polarizations**, $P_n^{NL} = P_n + c.c.$ $(n = \omega, 2\omega)$, for each of the frequency conversion processes are written as

$$P_{2\omega} = 2\varepsilon_0 d E_\omega^2, \quad \text{and} \quad P_\omega = 4\varepsilon_0 d E_{2\omega} E_\omega^*$$

The coupled-wave equations for the slow amplitudes are

$$\frac{dA_{2\omega}}{dz} = i\frac{2d\omega}{n(2\omega)c} A_\omega^2 e^{i\Delta kz}$$

$$\frac{dA_\omega}{dz} = i\frac{2d\omega}{n(\omega)c} A_{2\omega} A_\omega^* e^{-i\Delta kz}$$

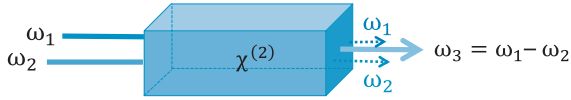
where $\Delta k = 2k_\omega - k_{2\omega}$ is the phase-matching condition. The **power conversion efficiency** from the wave at frequency ω (with input intensity I_ω^{in}) to the wave at frequency 2ω in the infinite plane wave approximation is

$$\eta_{2\omega} = \tanh^2(L/L_{NL}), \quad \text{where} \quad L_{NL} = \frac{1}{4\pi d}\sqrt{\frac{2\varepsilon_0 n_\omega^2 n_{2\omega} c\lambda_\omega^2}{I_\omega^{in}}}$$

Second-harmonic generation is commercially important. For example, the laser industry produces green 532-nm lasers using 1064-nm light and bulk KDP crystal. Second-harmonic generation can also be used for ultrashort-pulse measurement, second-harmonic generation microscopy, and characterization of crystalline materials.

Difference-Frequency Generation

Three-wave interactions, which take place in second-order nonlinear matter, result in an energy flow from the two fields with frequencies ω_1 and ω_2 to the difference-frequency $\omega_3 = \omega_1 - \omega_2$ field.



Difference-frequency generation can be considered as the inverse process to sum-frequency generation. Its nonlinear polarizations, $P_n^{NL} = P_n + c.c.$ $(n = 1, 2, 3)$, are

$$P_3 = 4\varepsilon_0 d E_1 E_2^*, \quad P_1 = 4\varepsilon_0 d E_3 E_2, \quad P_2 = 4\varepsilon_0 d E_3^* E_1$$

The coupled-wave equations for the slow amplitudes are

$$\frac{dA_1}{dz} = i\frac{2d\omega_1}{n(\omega_1)c} A_3 A_2 e^{-i\Delta kz}$$

$$\frac{dA_2}{dz} = i\frac{2d\omega_2}{n(\omega_2)c} A_3^* A_1 e^{i\Delta kz}$$

$$\frac{dA_3}{dz} = i\frac{2d\omega_3}{n(\omega_3)c} A_1 A_2 e^{i\Delta kz}$$

where $\Delta k = k_1 - k_2 - k_3$ are the phase-matching conditions. Difference-frequency generation is initiated by two pump beams of comparable intensities.

If the ω_1 beam (the pump beam) has high intensity and the ω_2 beam (the signal beam) has low intensity, the difference-frequency generation will cause amplification of the ω_2 beam. During this amplification process, the ω_3 beam (the idler) will be generated.

This process is known as **parametric amplification**. Placing highly reflecting mirrors at ω_2 and/or ω_3 on both sides of the sample, one can create a device known as an **optical parametric oscillator**. The first of such devices was built by Joseph Giordmaine and Robert Miller in 1965.

Phase-Matching Conditions

Phase matching matches the phase velocities of the desired wave to its driving, nonlinear-polarization wave. For example, consider second-harmonic generation, where the **phase-matching conditions** are $n(2\omega) - n(\omega) = 0$ and cannot be satisfied for normally dispersive materials.

Consider anisotropic materials, for example, **uniaxial crystals**, where, for each frequency, two normal modes with orthogonal polarizations propagate at different phase velocities. One of these waves (the **ordinary wave**) propagates with the **ordinary refractive index** n_o in all directions. The second wave (the **extraordinary wave**) propagates with an **extraordinary refractive index** $n_e(\theta)$, where θ is the angle between the direction of propagation and the principal axes of the crystal. Uniaxial crystals have a single axis of symmetry (the Z axis), which coincides with the principal optic axis. Thus, on the crystal principal axes (X, Y, Z), the principal refractive indices are $n_X = n_Y = n_o$ and $n_Z = n_e$.

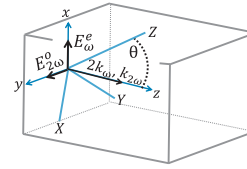
There are two types of angular phase matching. In *Type I*, the two incident waves have the *same polarization*. In *Type II*, these waves have *orthogonal polarizations*. Here we consider **Type I phase matching**.

In a **positive uniaxial crystal**, where $n_o < n_e$, phase matching can be attained by finding values of θ_p that satisfy the equation $n_o(2\omega) = n_e(\omega, \theta_p)$, or

$$\frac{1}{n_0^2(2\omega)} = \frac{1}{n_e^2(\omega, \theta_p)} = \frac{\cos^2\theta_p}{n_0^2(\omega)} + \frac{\sin^2\theta_p}{n_e^2(\omega)}$$

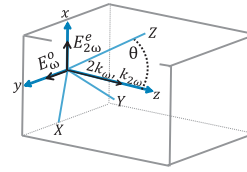
The solution to this equation is

$$\sin^2\theta_p = \frac{n_o^{-2}(\omega) - n_o^{-2}(2\omega)}{n_o^{-2}(\omega) - n_e^{-2}(\omega)}$$



In a **negative uniaxial crystal**, where $n_o > n_e$, phase matching can be attained by finding values of θ_p that satisfy the equation

$$\sin^2\theta_p = \frac{n_o^{-2}(\omega) - n_o^{-2}(2\omega)}{n_e^{-2}(2\omega) - n_o^{-2}(2\omega)}$$



Third-Order Nonlinear Optical Interactions

Third-order nonlinear processes are allowed in all media. In media with centrosymmetry, the second-order nonlinearity is absent, and the dominant nonlinearity is of the third order. If a monochromatic field $E(t) = E_\omega \cos(\omega t)$ is applied to a third-order nonlinear medium, its nonlinear polarization density will contain two components at the angular frequencies ω and 3ω:

$$P^{NL} = \frac{3}{4}\varepsilon_0 \chi^{(3)}(-\omega, \omega, \omega, -\omega)|E_\omega|^2 E_\omega \cos(\omega t) + \frac{1}{4}\varepsilon_0 \chi^{(3)}(-3\omega, \omega, \omega, \omega) E_\omega^3 \cos(3\omega t)$$

The first term in this relation describes a nonlinear contribution at the frequency of the incident field ω. Accounting for the linear polarization density $P^L = \varepsilon_0 \chi^{(1)} E_\omega \cos(\omega t)$, one can write the total polarization density at the frequency of the applied field as

$$P^{NL}(\omega) = \varepsilon_0(\chi^{(1)} + \tilde{\chi}^{(3)}|E_\omega|^2)E_\omega \cos(\omega t)$$

where $\tilde{\chi}^{(3)} = 3\chi^{(3)}(-\omega, \omega, \omega, -\omega)/4$. Since $P^{NL}(\omega)$ depends on $|E_\omega|^2$, the refractive index depends on $|E_\omega|^2$, too. Indeed, $n^2 = 1 + \chi^{(1)} + \tilde{\chi}^{(3)}|E_\omega|^2 = n_0^2 + \tilde{\chi}^{(3)}|E_\omega|^2$, where n_0 is the linear refractive index of the material. Thus, we have

$$n = n_0\sqrt{1 + \frac{\tilde{\chi}^{(3)}}{n_0^2}|E_\omega|^2} \cong n_0 + \frac{\tilde{\chi}^{(3)}}{2n_0}|E_\omega|^2 = n_0 + n_{2I} I_\omega$$

where an **optical constant** $n_{2I} = \tilde{\chi}^{(3)}/c\varepsilon_0 n_0^2$ characterizes the strength of the optical nonlinearity. This dependance is known as the **optical Kerr effect**.

The second term in the polarization density of the third-order nonlinear medium,

$$P^{NL}(3\omega) = \frac{1}{4}\varepsilon_0 \chi^{(3)}(-3\omega, \omega, \omega, \omega) E_\omega^3 \cos(3\omega t)$$

is responsible for **third-harmonic generation**, or **frequency tripling**.

Self-Focusing

One of several effects associated with the **optical Kerr effect** is **self-focusing** or an induced lens effect. Consider a single-mode laser beam with a Gaussian transverse profile propagating in a third-order nonlinear medium with a refractive index

$$n = n_0 + n_{2I} I_\omega$$

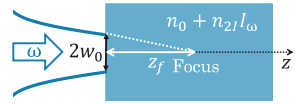
If $n_{2I} > 0$, the central part of the beam, which has higher intensity, will experience a larger refractive index than the edge and will propagate at a slower velocity than at the edge. The original plane wavefront of the beam will undergo a distortion similar to that imposed on the beam by a positive lens.

We assume that the Gaussian laser beam propagates in the sample. Its waist $2w_0$ is located at the input face. One can estimate the distance to the focus z_f following the **Fermat principle**, which states that the optical path lengths (OPLs) between the input face of the sample and the focus are the same for the central and peripheral rays. For the central ray, the OPL is $z_f(n_0 + \delta n)$. We assume that $\delta n = n_{2I} I_\omega^{\max}$, where $I_\omega^{\max}$ is the maximum intensity of the pump beam. For the peripheral ray, the OPL can be estimated as $\sqrt{w_0^2 + z_f^2}(n_0 + \delta n/2)$. Equating the OPLs for the central and peripheral rays, one obtains the equation

$$z_f(n_0 + \delta n) = \sqrt{w_0^2 + z_f^2}(n_0 + \delta n/2)$$

Approximating the right part of this equation, one obtains

$$z_f \cong w_0 \sqrt{\frac{n_0}{\delta n}} = w_0 \sqrt{\frac{n_0}{n_{2I} I_\omega^{\max}}}$$



A beam with a finite cross section undergoes diffraction, which is inversely proportional to the square of the beam radius. These effects compete with each other. When the beam spread caused by diffraction is completely compensated by self-focusing, **self-trapping** may occur. In this case, the beam can propagate over a long distance without any change in its diameter.

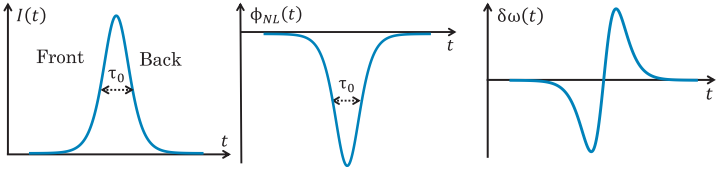
Self-Phase Modulation

The second effect associated with the **optical Kerr effect** is **self-phase modulation**, which is the change in the phase of an optical pulse due to the nonlinearity of the refractive index of the medium. Self-phase modulation is based on the fact that the spectral content of the pulse becomes modified during its propagation in nonlinear material. Consider the propagation of the pulse $E(z,t) = A(z,t)e^{i(k_0 z - \omega_0 t)} + c.c.$ in a medium with a nonlinear refractive index $n = n_0 + n_{2I}I$, where $I(t) = (n_0 c/2\pi)|A(z,t)|^2$. The phase of the transmitted pulse changes according to

$$\phi_{NL}(t) = -k_0 n_{2I} I(t) L$$

where $k_0 = \omega_0/c$, and L is the length of the sample. We define the **instantaneous frequency** as

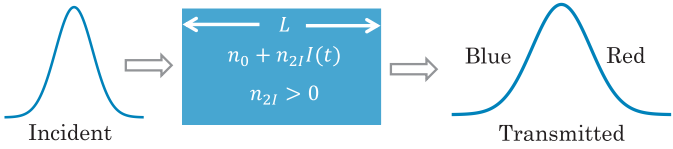
$$\omega(t) = \omega_0 + \delta\omega(t), \text{ where } \delta\omega(t) = \frac{d}{dt}\phi_{NL}(t)$$



The leading edge of the pulse has a negative slope, its peak has a zero slope, and its trailing edge has a positive slope. Thus, the pulse's leading edge is red-shifted, the frequency shift near the peak of the pulse is zero, and the trailing edge of the pulse is blue-shifted. If a pulse with an intensity amplitude I_0 rises and falls within τ_0, the maximum frequency shift is

$$\delta\omega_{\max} \cong \Delta\phi_{NL}^{\max}/\tau_0, \text{ where } \Delta\phi_{NL}^{\max} \cong k_0 n_{2I} I_0 L$$

The bandwidth of the pulse is τ_0^{-1}, and self-phase modulation becomes important for $\Delta\phi_{NL}^{\max} \geq 2\pi$.



Solitons

Consider a pulse propagating in a nonlinear medium with a frequency-dependent dielectric function. Its propagation constant, which depends on both the frequency and the intensity of the optical wave, can be presented as a truncated power series expansion of the form

$$k = k_0 n_0(\omega_0) + k_1(\omega - \omega_0) + \frac{1}{2}k_2(\omega - \omega_0)^2 + \Delta k_{NL}$$

where $n_0(\omega_0)$ is the linear refractive index at the frequency ω_0, and $\Delta k_{NL} = k_0 \Delta n_{NL} = k_0 n_{2I} I$ is the nonlinear contribution. The constant k_1 is given as

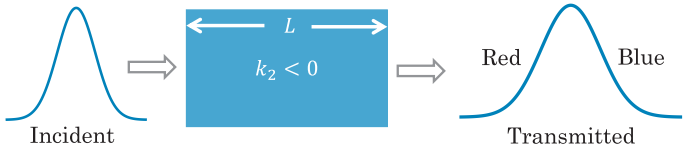
$$k_1 = \left(\frac{dk}{d\omega}\right)_{\omega=\omega_0} = \frac{1}{c}\left(n_0(\omega) + \omega\frac{d}{d\omega}n_0(\omega)\right)_{\omega=\omega_0} = \frac{1}{v_g(\omega)}$$

where $v_g(\omega)$ is the **group velocity**, which describes the rate at which the energy of the pulse or its envelope moves.

$$k_2 = \left(\frac{d^2k}{d\omega^2}\right)_{\omega=\omega_0} = \frac{d}{d\omega}\left(\frac{1}{v_g(\omega)}\right)_{\omega=\omega_0} = \left(-\frac{1}{v_g^2}\frac{dv_g}{d\omega}\right)_{\omega=\omega_0}$$

is a measure of the **group velocity dispersion**.

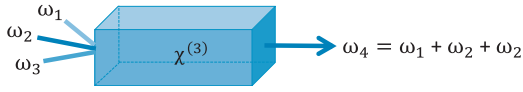
If $k_2 < 0$, the pulse components with higher frequencies propagate faster than the low-frequency components, and vice versa. As a result, pulses propagating in linear media undergo *broadening*.



In a nonlinear medium ($\Delta n_{NL} \neq 0$) the situation changes. If $\Delta n_{NL} > 0$, the leading edge of the pulse has a lower frequency than the trailing edge. Thus, the leading edge travels more slowly than the trailing edge, and the pulse *shrinks*. This pulse-narrowing effect increases as the pulse intensity increases. If narrowing is precisely compensated by broadening, the pulse can propagate without any change in shape. Such pulses are known as **solitons**.

Four-Wave Mixing

Four-wave mixing is the interaction of four waves in a nonlinear medium via third-order polarization. There are different schemes of four-wave mixing.



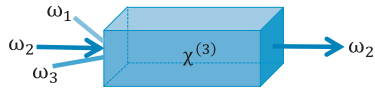
Three input pump waves propagating at different frequencies, ω_1, ω_2, and ω_3, can generate an output wave at the frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$. Assume that three pump waves, $\vec{E}_n(\omega_n) = \vec{A}_n e^{i(\vec{k}_n\vec{r}-\omega_n t)} + c.c.$, with different frequencies, propagate in a third-order nonlinear isotropic medium. Here $n = 1, 2, 3$, and A_n is a constant. $|\vec{k}_n| = \omega_n n(\omega_n)/c$, where $n(\omega_n)$ is the refractive index at frequency ω_n. The output field $\vec{E}_4(\omega_4) = \vec{A}_4 e^{i(\vec{k}_4\cdot\vec{r}-\omega_4 t)} + c.c.$ at frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ can be obtained using the nonlinear wave equation:

$$\nabla \times \nabla \times \vec{E}_4 - \frac{\omega_4^2}{c^2}\varepsilon\vec{E}_4 = \mu_0\omega_4^2\vec{P}_4^{NL}$$

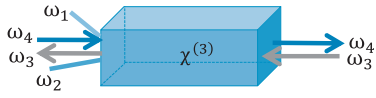
where

$$\vec{P}_4^{NL} = \chi^{(3)}(\omega_4) : \vec{E}(\omega_1)\vec{E}(\omega_2)\vec{E}(\omega_3)$$

is the **third-order polarization**. As in the case of the second-order nonlinear medium, we can use the slowly varying amplitude approximation. In a third-order medium, **phase matching** $\Delta\vec{k} = \vec{k}_1 + \vec{k}_2 + \vec{k}_3 - \vec{k}_4 = 0$ can be achieved by properly adjusting the direction of propagation of the three pump beams.



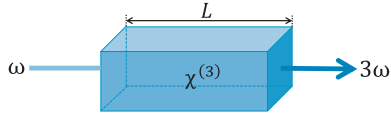
The output field can propagate at the same frequency (ω_2) as one of the input fields. In this case, the input field at ω_2 experiences a gain or loss.



Two strong incident waves at ω_1 and ω_2 can act as the pump sources. Two counter-propagating weak waves, the signal (ω_3) and idler (ω_4) waves, can be amplified.

Third-Harmonic Generation

Consider the case in which three pump waves at the same frequencies ω propagate in a third-order nonlinear isotropic medium. The output wave will have frequency 3ω. This special case of four-wave mixing is known as **third-harmonic generation**.



In crystals with inversion symmetry, second-harmonic generation is forbidden in the context of the electric dipole approximation, but third-harmonic generation is allowed. The theory of third-harmonic generation is similar to that of second-harmonic generation. It is also based on the same nonlinear wave equation, but second-order nonlinear polarization must be replaced by third-order nonlinear polarization. Consider a plane wave $E_n(z,t) = A_n e^{i(k_n z - \omega_n t)} + c.c.$ propagating in the z direction. As in the case of second-harmonic generation, we use the slowly varying-amplitude approximation for the amplitudes $|\frac{d^2A_n}{dz^2}| < |k_n \frac{dA_n}{dz}|$. The coupled-wave equations will have the form

$$\frac{dA_{3\omega}}{dz} = i\frac{3\chi^{(3)}\omega}{2n(3\omega)c}A_\omega^3 e^{i\Delta kz}$$

$$\frac{dA_\omega}{dz} = i\frac{3\chi^{(3)}\omega}{2n(\omega)c}A_{3\omega}(A_\omega^*)^2 e^{-i\Delta kz}$$

where $\Delta k = 3k_\omega - k_{3\omega}$ is the **phase matching**, which is difficult to achieve in solids. Using the coupled-wave equations, and assuming perfect phase matching and a nondepleted pump, one can calculate the **efficiency of third-harmonic generation** as

$$\eta = \frac{I_{3\omega}(L)}{I_\omega(0)} = 36\pi^2\left(\frac{L}{\lambda}\right)^2 \frac{(\chi^{(3)})^2 I_\omega^2(0)}{n(3\omega)n^3(\omega)\varepsilon_0^2 c^2}$$

Typically, the efficiency of third-harmonic generation is very small: $\eta \ll 1$.

Spontaneous Raman Scattering

Photons incident on a medium can be scattered by the atoms within the medium. If energy and momentum exchanges with excitations associated with the atoms (e.g., phonons) take place in the system, the scattered photons have energies and directions that differ from those of the incident photons. The scattering process can be considered as the absorption of an incident photon accompanied by an excitation of the electronic distribution of an atom. The electronic de-excitation process results in the emission of another photon. Inelastic photon scattering can take place only if there is a change in *electronic polarizability*.

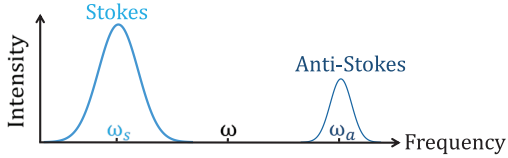
Light scattering from optical phonons is known as **Raman scattering**. If $E = E_0 \cos(\omega t)$ is the magnitude of the electric field of an incident light, the polarization density is $P = \varepsilon_0 \chi E$. The electronic susceptibility χ is a function of the nuclear coordinates. Any phonon excitation results in atomic displacement u. It will perturb χ, which can be presented as a Taylor series:

$$\chi = \chi_0 + \left(\frac{\partial \chi}{\partial u}\right) u + \frac{1}{2}\left(\frac{\partial^2 \chi}{\partial u^2}\right) u^2 + \ldots$$

We can present the displacement as $u = u_0 \cos(\omega_q t)$. In this case, the polarization density is written as

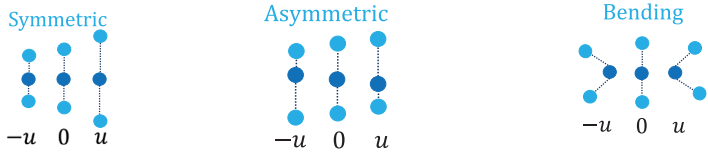
$$P \approx \varepsilon_0 \chi_0 E + \varepsilon_0 \left(\frac{\partial \chi}{\partial u}\right) u_0 E_0 \{\cos(\omega - \omega_q)t + \cos(\omega + \omega_q)t\}$$

The first term here describes elastic scattering. The scattering wave has the same frequency as the incident wave (**Rayleigh scattering**). The second and third terms describe inelastic (**Raman**) scattering at frequencies $\omega_s = \omega - \omega_q$ (**Stokes scattering**) and $\omega_a = \omega + \omega_q$ (**anti-Stokes scattering**), respectively. Raman scattering is possible only if $\partial \chi / \partial u \neq 0$, i.e., with the participation of Raman-active phonons.



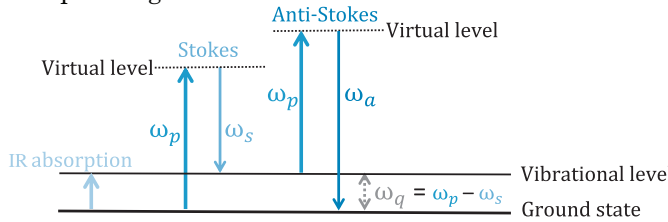
Raman-Active Phonons

Not all vibrational modes can participate in Raman scattering. For example, consider the vibrational modes of a linear triatomic molecule. These modes include the symmetric (in-phase) stretch mode, the asymmetric (out-of-phase) stretch mode, and the bending modes.



The asymmetrical stretch and bending modes have a symmetric polarizability α change; as a result, $\partial\alpha/\partial u = 0$ for these modes. They are not Raman active, meaning that they cannot participate in Raman scattering; they can only be involved in IR absorption. Only the symmetrical mode with $\partial\alpha/\partial u \neq 0$ is the **Raman-active mode**, which can participate in Raman scattering.

Raman Stokes scattering consists of a transition from the ground state to a virtual level as a result of pump photon absorption, followed by a transition from the virtual level to a vibrational excited state accompanied by Stokes photon generation. **Raman anti-Stokes scattering** consists of a transition from the excited vibrational level to a virtual level as a result of pump photon absorption, followed by a transition from the virtual level to the ground state accompanied by anti-Stokes photon generation.

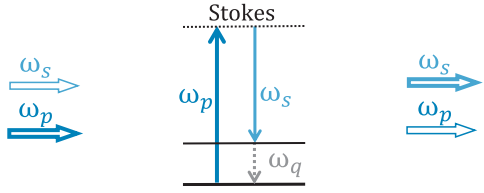


Spontaneous Raman scattering is a very weak process. The anti-Stokes lines are much weaker than the Stokes lines because in thermal equilibrium the population of the excited level is much smaller than the population of the ground level. Their intensities are associated with the Boltzmann factor as

$$I(\omega_a)/I(\omega_s) = e^{(-\hbar\omega_q/\kappa_B T)}$$

Stimulated Raman Scattering

The Raman scattering strength can be enhanced with a stimulating laser operating at the Stokes or anti-Stokes wavelength. This scattering process is known as **stimulated Raman scattering**.



Consider the case where the incident electric field, $E(z,t) = \frac{1}{2}[A_p e^{i(k_p z - \omega_p t)} + A_s e^{i(k_s z - \omega_s t)} + c.c.]$, consists of the pump ($\omega_p$) and Stokes ($\omega_s$) waves. It induces a dipole moment p, which can be expressed in terms of the molecular polarizability α as $p = \varepsilon_0 \alpha(u) E$, where $\alpha(u) \approx \alpha_0 + (\frac{du}{d\alpha})u$. The potential energy of a polarized molecule is $W = -pE/2$. Its equation of motion has the form

$$\frac{\partial^2 u}{\partial t^2} + 2\gamma \frac{\partial u}{\partial t} + \omega_0^2 u = -F\frac{1}{m}$$

where ω_0 is the resonance frequency, m is the mass of the molecule, γ is the damping coefficient, and $F = -\nabla_u W = \frac{\varepsilon_0}{2}(\frac{du}{d\alpha})E^2$ is the force, which is the gradient of the potential energy W. We can write the displacement as $u(z,t) = \frac{1}{2}u_\omega e^{i[(k_p - k_s)z - (\omega_p - \omega_s)t]} + c.c.$ Substituting $u(z,t)$ into the equation of motion, and considering only the resonant terms, we obtain the relation

$$u_\omega = -\frac{\varepsilon_0 (d\alpha/du) A_p A_s^*}{4m\omega_0(\omega_p - \omega_s - \omega_0 + i\gamma)}$$

Here, the approximation $\omega_0^2 - \omega_q^2 - i2\gamma\omega_q \approx 2\omega_0(\omega_0 - \omega_q - i\gamma)$ has been accounted for. Again, considering only resonant terms, the induced nonlinear polarization is

$$P_{NL} = Np_{NL} \approx N\varepsilon_0\left(\frac{du}{d\alpha}\right)uE \approx \frac{1}{2}[P_{\omega_p}^{NL} e^{-i\omega_p t} + P_{\omega_s}^{NL} e^{-i\omega_s t} + c.c.]$$

where N is the molecular density.

Stimulated Raman Scattering (cont.)

The polarization components $P^{NL}_{\omega_p}$ and $P^{NL}_{\omega_s}$ oscillate at the pump (ω_p) and Stokes (ω_s) frequencies, respectively. They can be calculated using the relations for the input electric field $E(z,t)$ and the displacement $u(z,t)$ and are written as

$$P^{NL}_{\omega_{p,s}} = -\frac{\varepsilon_0^2 N(d\alpha/du)^2 |A_{s,p}|^2 A_{p,s}}{8m\omega_0(\omega_p - \omega_s - \omega_0 \pm i\gamma)} e^{ik_{p,s}z}$$

Here the "+" sign in "±" corresponds to the polarization at frequency ω_p, and the "−" sign in "±" corresponds to the polarization at frequency ω_s. Alternatively, the third-order polarization can be presented as

$$P^{NL}_{\omega_p} = \frac{3\varepsilon_0 \chi^{(3)}_p}{2} |E_s|^2 E_p e^{ik_p z}, \text{ and } P^{NL}_{\omega_s} = \frac{3\varepsilon_0 \chi^{(3)}_s}{2} |E_p|^2 E_s e^{ik_s z}$$

Comparing the relations for $P^{NL}_{\omega_p}$ and $P^{NL}_{\omega_s}$, one obtains the relation for the **nonlinear susceptibility**:

$$\chi^{(3)}_p = [\chi^{(3)}_s]^* = -\frac{\varepsilon_0 N(d\alpha/du)^2}{12m\omega_0(\omega_q - \omega_0 + i\gamma)}$$

Using the slowly varying-amplitude approximation for the amplitudes of the pump and Stokes waves $|\frac{d^2A_i}{dz^2}| \ll |k_i \frac{dA_i}{dz}|$, where $i = p, s$, one obtains the system of coupled-wave equations:

$$\frac{dA_p}{dz} = i\frac{3\omega_p^2}{4k_p c^2}\chi_s^* |A_s|^2 A_p, \text{ and } \frac{dA_s}{dz} = i\frac{3\omega_s^2}{4k_s c^2}\chi_s |A_p|^2 A_s$$

Considering the nondepleted pump signal I_p, one can obtain a relation that describes the exponential growth of the intensity of the Stokes signal:

$$I_s(z) = I_s^{in} e^{g_R I_p z}, \text{ where } g_R = \frac{3\omega_s \text{Im}(\chi_3)}{2\varepsilon_0 n_p n_s c^2}$$

Here I_s^{in} in the input Stokes intensity, and g_R is the **gain factor**.

Spontaneous Brillouin Scattering

Spontaneous Brillouin scattering is the scattering of an incident electromagnetic wave by acoustic phonons, which are pressure or density waves that are present in the medium. This scattering is linked to a fluctuation in the dielectric constant of the medium, which is caused by a change in the mass density of the medium, according to

$$\Delta\varepsilon = \frac{\partial\varepsilon}{\partial\rho}\Delta\rho$$

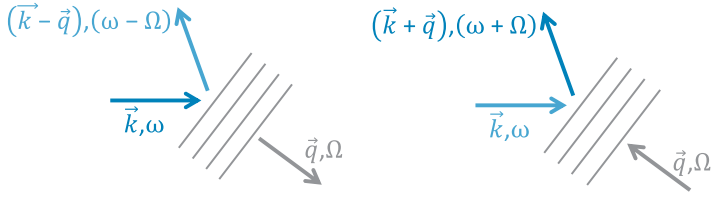
where $\Delta\varepsilon$ and $\Delta\rho$ are the changes in dielectric constant and density, respectively. The density fluctuation is related to pressure $\tilde{p}$ and entropy S, according to

$$\Delta\rho = \left(\frac{\partial\rho}{\partial\tilde{p}}\right)_S \Delta\tilde{p} + \left(\frac{\partial\rho}{\partial S}\right)_{\tilde{p}} \Delta S$$

Entropy fluctuations ΔS result in **Rayleigh scattering**, i.e., scattering without a frequency shift in the scattered wave. Spontaneous Brillouin scattering can be considered as a Doppler-shifted reflection from an acoustic wavefront. We assume here that the acoustic wave propagating in the medium has the form $\Delta\tilde{p}(\vec{r},t) = \Delta\tilde{p}_0 e^{i(\vec{q}\cdot\vec{r}-\Omega t)} + c.c.$ In this case, the magnitude of the incident electric field, $E(z,t) = E_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} + c.c.$, induces nonlinear polarization:

$$\begin{aligned} P(\vec{r},t) = \varepsilon_0\Delta\chi E = \Delta\varepsilon E &= \frac{\partial\varepsilon}{\partial\rho}\left(\frac{\partial\rho}{\partial\tilde{p}}\right)_S \Delta\tilde{p}E \\ &= \frac{\partial\varepsilon}{\partial\rho}\left(\frac{\partial\rho}{\partial\tilde{p}}\right)_S [\Delta\tilde{p}_0^* E_0 e^{i[(\vec{k}-\vec{q})\cdot\vec{r}-(\omega-\Omega)t]} \\ &\quad + \Delta\tilde{p}_0 E_0 e^{i[(\vec{k}+\vec{q})\cdot\vec{r}-(\omega+\Omega)t]}] \end{aligned}$$

which results in the generation of Stokes and anti-Stokes waves at frequencies $(\omega-\Omega)$ and $(\omega+\Omega)$, and with the wave vectors $(\vec{k}-\vec{q})$ and $(\vec{k}+\vec{q})$, respectively.

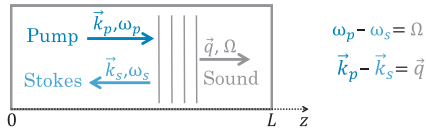


Stokes scattering Anti-Stokes scattering

Principals of Stimulated Brillouin Scattering

Stimulated Brillouin scattering, which is much more efficient than spontaneous scattering, is a result of parametrical coupling between electromagnetic and acoustic waves. It is based on light scattering caused by two different physical mechanisms:

- **Electrostriction** is the deformation (compression or tension) of a solid under an applied electric filed.
- **Optical absorption** heats the regions of high field strength in lossy optical media, causing those regions to expand.



Consider the more commonly used **electrostrictive stimulated Brillouin scattering**. Assume that three waves are present in an isotropic medium: the pump wave $(\omega_p,\vec{k}_p)$, the acoustic wave $(\Omega,\vec{q})$, and the Brillouin Stokes scattered wave $(\omega_s,\vec{k}_s)$. The optical field within the medium has the form $E(z,t) = E_p(z,t) + E_s(z,t)$, where the pump field is $E_p(z,t) = A_p e^{i(k_p z-\omega_p t)} + c.c.$, and the Stokes field is $E_s(z,t) = A_s e^{i(k_s z-\omega_s t)} + c.c.$. The acoustic wave in terms of the material density can be described as $\rho(z,t) = \rho_0 + (\Delta\rho(z,t)e^{i(qz-\Omega t)} + c.c.)$, where ρ_0 is the average density of the medium. The acoustic wave must satisfy the equation

$$\frac{\partial^2\rho}{\partial t^2} - \Gamma'\nabla^2\frac{\partial\rho}{\partial t} - \upsilon\nabla^2\rho = -\nabla\cdot\vec{f}$$

where $\vec{f} = \frac{1}{2}\gamma_e\nabla\langle E_p E_s\rangle$ is the electrostrictive force, $\gamma_e = \rho\frac{\partial\varepsilon}{\partial\rho}$ is the electrostrictive coefficient, Γ' is a damping parameter, and υ is the velocity of the sound. Using this equation, assuming steady-state conditions and dropping the spatial derivative term, one can obtain the sound wave amplitude $\Delta\rho(z,t)$, which can be used to calculate the nonlinear polarization as

$$P_{NL} = \varepsilon_0\frac{\gamma_e}{\rho_0}\rho(z,t)E(z,t)$$

Stimulated Brillouin Scattering

Nonlinear polarization has two components oscillating at the pump ω_p and the Stokes ω_s frequencies:

$$P_{NL} = \varepsilon_0 \frac{\gamma_e}{\rho_0} \Delta\rho A_s e^{i(k_s z - \omega_s t)} + \varepsilon_0 \frac{\gamma_e}{\rho_0} \Delta\rho^* A_p e^{i(-k_p z - \omega_p t)}$$

$\Delta\rho = \gamma_e q^2 \frac{A_p A_s^*}{\Omega_B^2 - \Omega^2 - i\Omega\Gamma_B}$ is the **acoustic wave amplitude**.

$\Omega_B = \frac{2n_p v}{c}\omega_p$ is the Brillouin frequency, n_p is the refractive index at frequency ω_p, and $\Gamma_B = q^2\Gamma'$ is the Brillouin linewidth.

Substituting the relation for nonlinear polarization into the wave equation, and considering steady-state conditions $(\partial/\partial t = 0)$ and the slowly varying-amplitude approximations $|\frac{d^2 A_i}{dz^2}| \ll |k_i \frac{dA_i}{dz}|$, where $i = p, s$, one obtains the system of coupled-amplitude equations:

$$\frac{dA_p}{dz} = i\frac{3\omega_p}{n_p c}\chi_B^{(3)}|A_s|^2 A_p$$

$$\frac{dA_s^*}{dz} = i\frac{3\omega_s}{n_s c}\chi_B^{(3)}|A_p|^2 A_s^*$$

$\chi_B^{(3)} = \left(\frac{\gamma_e^2 n_p \omega_p}{6\varepsilon_0 \rho_0 c v}\right) \frac{1}{\Omega_B - \Omega - i\Gamma_B/2}$ is the **Brillouin susceptibility**.

The coupled equations for the intensities of the two interacting optical waves are written as

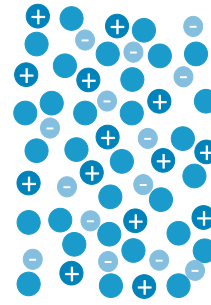
$$\frac{dI_p}{dz} = -g_B^e I_p I_s \text{ and } \frac{dI_s}{dz} = -g_B^e I_p I_s$$

$g_B^e = \frac{\gamma_e^2 \omega_p^2}{\varepsilon_0^2 \rho_0 n_s v c^3 \Gamma_B} \frac{(\Gamma_B/2)^2}{(\Omega_B - \Omega)^2 + (\Gamma_B/2)^2}$ is the **Brillouin gain factor**.

Considering the nondepleted pump signal I_p, one can obtain the relation for the exponentially growing Stokes intensity:

$$I_s(z) = I_s(L) e^{g_B^e I_p (L - z)}$$

The Debye–Hückel Length

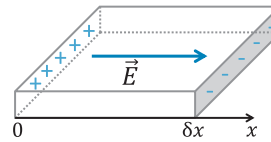


The term *plasma* was introduced by Lewi Tonks and Irving Langmuir in 1929. It comes from the Greek πλασμα and means *moldable substance*. A **plasma** is a state of matter in which all or a considerable number of atoms have lost one or several of their electrons and have become a mixture of free electrons and positive ions, which interact with one another through Coulomb forces.

The internal energy of a plasma consists of the kinetic energies of the electrons and ions, and of their Coulomb interaction energy. Here, we perturb a slab of a plasma by shifting electrons a distance x. The built-up charge is $en_e x$ per unit area, where n_e is the electron density. The magnitude of the generated electric field is

$$E = |\vec{E}| = -en_e x/\varepsilon_0$$

The gain in potential energy of a charged particle after moving a distance δx through the space-charge layer is



$$W_{\text{pot}} = -\int_0^{\delta x} eEdx = \frac{e^2 n_e (\delta x)^2}{2\varepsilon_0}$$

Since the mean energy associated with a degree of freedom is $\kappa_B T_e/2$, we can estimate deviations from quasi-neutrality on a scale defined by $W_{\text{pot}} = \kappa_B T_e/2$. This relation gives us a charge separation over the so-called **Debye–Hückel length**:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \kappa_B T_e}{e^2 n_e}}$$

The Coulomb potential is screened by the medium over the distance λ_D.

Plasma Permittivity

The equation of motion of an electron,

$$m_e \frac{d^2x}{dt^2} = eE, \quad \text{i.e.,} \quad \frac{d^2x}{dt^2} + \left(\frac{n_e e^2}{\varepsilon_0 m_e}\right) x = 0$$

corresponds to the equation of motion of the harmonic oscillator with frequency

$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e}} \quad (\text{the } \textbf{plasma frequency}).$$

Consider a plane electromagnetic wave of frequency ω ($\omega > \omega_p$) propagating through a plasma. The wave electric field has the form $E(t) = E_0 e^{-i\omega t} + E_0^* e^{i\omega t}$. The equation of motion of an electron in this electric field is

$$\frac{d^2x}{dt^2} + \nu \frac{dx}{dt} = \frac{eE(t)}{m_e}$$

where ν is the collision frequency. From this equation, we can obtain the relation $x(t) = x_0 e^{-i\omega t} + x_0^* e^{i\omega t}$ with amplitude $x_0 = -eE_0/m_e\omega(\omega + i\nu)$. Since ex_0 is the amplitude of the electric dipole moment per electron, the **plasma susceptibility** $\chi(\omega)$ can be calculated using the equation $\varepsilon_0 \chi(\omega) E_0 = e n_e x_0$. It has the form

$$\chi(\omega) = -\frac{{\omega_p}^2}{\omega(\omega + i\nu)}$$

The **plasma permittivity** is written as

$$\varepsilon(\omega) = \varepsilon_0[1 + \chi(\omega)] = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

where

$$\varepsilon'(\omega) = \varepsilon_0\left[1 - \frac{{\omega_p}^2}{(\omega^2 + \nu^2)}\right], \quad \text{and} \quad \varepsilon''(\omega) = \varepsilon_0 \frac{\nu}{\omega} \frac{{\omega_p}^2}{(\omega^2 + \nu^2)}$$

Here $\varepsilon''(\omega)$ describes energy loss associated with heat generation.

Electromagnetic Waves in a Plasma

In a high-frequency plasma ($\omega \gg \nu$), the plasma permittivity has the form

$$\varepsilon(\omega) = \varepsilon_0 n^2 \approx \varepsilon_0\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

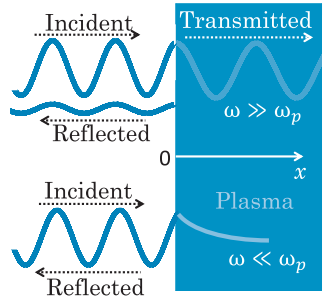
Consider a plane wave of frequency ω ($\omega > \omega_p$) propagating through the high-frequency plasma. Suppose that the magnitude of the electric field has the form $E = E_0 e^{i(kx-\omega t)}$. The phase velocity of the wave in the medium is $v_p = \frac{\omega}{k} = \frac{c}{n}$; i.e., the **plasma dispersion relation** has the form

$$\omega^2 = k^2c^2 + \omega_p^2$$

According to this dispersion relation, the **phase velocity** of the high-frequency waves v_p and the **group velocity** of the wave pulse v_g propagating through a plasma, respectively, are

$$v_p = \frac{\omega}{k} = \frac{c}{\sqrt{1 - \omega_p^2/\omega^2}} \quad \text{and} \quad v_g = \frac{d\omega}{dk} = c\sqrt{1 - \frac{\omega_p^2}{\omega^2}}$$

If $\omega < \omega_p$, both the phase velocity and the group velocity become imaginary. The wave *attenuates* as it propagates. The associated wavenumber is $k = i\sqrt{\omega_p^2 - \omega^2}/c = i\tilde{k}$. The electric field magnitude has the form $E = E_0 e^{-\tilde{k}x} e^{-i\omega t}$. In this case, the electromagnetic wave incident on a plasma will not propagate through the plasma; it will be *totally reflected*. This wave forms a decaying *standing wave* in the plasma. For $\omega < \omega_p$, the plasma is *opaque*, and for $\omega > \omega_p$, it is *transparent*.



The electron density n_e, for which $\omega = \omega_p$, is known as the **critical electron density** n_e^c.

A Short History of Optical Pressure

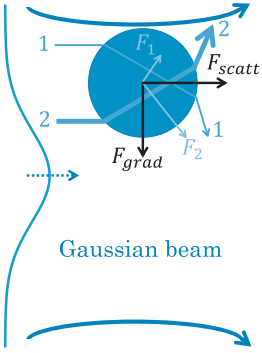
- In 1619 Johannes Kepler, who was a key figure of the Scientific Revolution of the 17th century and was known for his laws of planetary motion, introduced the concept of **radiation pressure** to explain the observation that a comet tail always points away from the Sun.
- In 1862, following the EM theory developed by Maxwell, it was accepted that electromagnetic radiation is associated with linear momentum. It exerts a pressure on a surface that is exposed to it.
- In 1901 Peter Lebedev and Ernest Nichols experimentally proved the existence of radiation pressure *qualitatively*. In 1903, Nichols and Gordon Hull proved the existence of radiation pressure *quantitatively*.
- In 1970, Arthur Ashkin guided particles with a weakly focused laser beam. He used microparticles with a refractive index higher than the surroundings. He observed the acceleration of particles by the **radiation force** and the pulling of particles towards the beam axis by a **gradient force**. Ashkin proposed and demonstrated the concept of **counter-propagating optical trapping**.
- In 1971, Arthur Ashkin and Joseph Dziedzic demonstrated the **optical levitation trap**. In this trap, gravitational forces counteract radiation pressure. Optical forces have also been complemented by hydrodynamic, acoustic, and electric forces.
- In 1986, a **single-beam gradient force trap** (**optical tweezers**) was demonstrated by Arthur Ashkin and his colleagues. This experiment was a breakthrough in the field of optical micromanipulation.

Since Ashkin's first experiment, optical forces have been used to develop optical stretchers, holographic optical tweezers, plasmonic tweezers, optical sorters, optical picotensiometers, optical conveyor belts, optical grippers, optical tractor beams, etc.

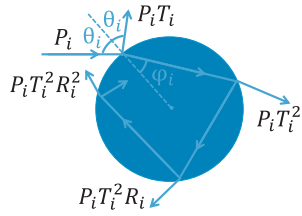
Optical Force in the Ray Optics Regime

Three different approaches can be used for optical force calculation, depending on the size of the particles compared to the wavelength of the laser beam.

- If the radius r of the particle is much larger than the light wavelength λ ($r > 20\lambda$), diffractive effects can be neglected. In this case, **geometrical optics** (ray optics) can be used for the optical force calculation.
- If the particle radius is comparable to the light wavelength ($r \sim \lambda$), the wave's **EM scattering** should be considered.
- If the particle radius is much smaller than the light wavelength ($r \ll \lambda$), **dipole approximation** can be used.



Consider a high-refractive-index transparent sphere illuminated by a Gaussian beam in terms of geometrical optics. A pair of light rays propagate in the medium with refractive index n_m and strike the particle symmetrically with respect to its center, but they have different intensities. The rays refract through the particle and produce the forces F_1 and F_2. The sum of the longitudinal components of these forces produces the **scattering force** F_{scatt} in the direction of the beam. The transversal component of F_1 is smaller than that of F_2 due to the laser beam intensity profile. The resulting transversal **gradient force** F_{grad} points toward the high-intensity region:



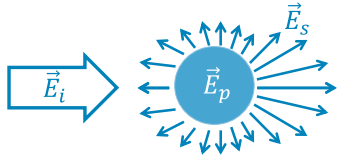
$$F_{\text{scatt}} = \sum_i^N \frac{n_m P_i}{c}\left[1 + R_i\cos(2\theta_i) - \frac{T_i^2[\cos(2\theta_i - 2\varphi_i) + R_i\cos(2\theta_i)]}{1 + R_i^2 + 2R_i\cos(2\varphi_i)}\right]$$

$$F_{\text{grad}} = \sum_i^N \frac{n_m P_i}{c}\left[1 + R_i\sin(2\theta_i) - \frac{T_i^2[\sin(2\theta_i - 2\varphi_i) + R_i\cos(2\theta_i)]}{1 + R_i^2 + 2R_i\cos(2\varphi_i)}\right]$$

Here, P_i, R_i, and T_i are power, reflection, and transmission coefficients of the i^{th} ray, respectively.

Optical Trapping as Scattering

Consider a homogeneous, optically linear, isotropic particle of diameter $d \approx \lambda$, where λ is the wavelength of the incident light. If the particle size is on the order of the wavelength of the **trapping laser light**, and if quantitatively precise results are required, the light fields need to be described in terms of Maxwell's equation.



For particles of diameter $d \approx \lambda$, a rigorous description of optical tweezers is based on the classical Mie theory, which is applied to spheres of arbitrary size. The original Mie theory, which was developed by Gustav Mie in 1908, is restricted to *plane-wave* illumination. This case is not applicable to **optical tweezers**. The theory, which describes arbitrary illumination, including Gaussian or Laguerre–Gaussian beams, is known as the **generalized Lorenz–Mie theory**. The incident light field can be expanded as an infinite series of the **vector spherical harmonics** as

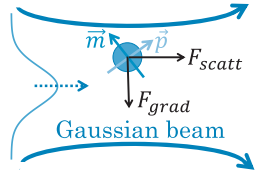
$$\vec{E}_i = \sum_{m=0}^{\infty} \sum_{n=m}^{\infty} \left(b_{emn} \vec{M}_{emn} + b_{omn} \vec{M}_{omn} + a_{emn} \vec{N}_{emn} + a_{omn} \vec{N}_{omn} \right)$$

where b_{emn}, b_{omn}, a_{emn}, and a_{omn} are expansion coefficients. Using the orthogonality of the vector harmonics and the finiteness of the incident field at the origin, and accounting for the boundary conditions between the sphere and the surrounding medium for the electric and corresponding magnetic fields, which are written as

$$\left(\vec{E}_i + \vec{E}_s - \vec{E}_p \right) \times \hat{e}_r = \left(\vec{H}_i + \vec{H}_s - \vec{H}_p \right) \times \hat{e}_r = 0$$

one obtains the scattered field $(\vec{E}_s, \vec{H}_s)$ and the field inside the particle $(\vec{E}_p, \vec{H}_p)$. Here, $\hat{e}_r$ is the radial unit vector. Considering the angular momentum of the incident and scattered light, one can calculate the force and torque acting on the particle.

Optical Force in the Rayleigh (Dipole) Approximation



If a particle radius r is much smaller than the wavelength λ of the incident light ($r \ll \lambda$), the responses of the particle to the incident light can be represented by an electric dipole $\vec{p}$ and a magnetic dipole $\vec{m}$ (the **Rayleigh** or **dipole approximation**).

According to the Mie theory, the field scattered by the particle can be calculated by summing up the contributions of all vector spherical harmonics with the Mie expansion coefficients a_ν and b_ν, where $\nu = 1, 2, 3\ldots$. If the first electric and magnetic coefficients a_1 and b_1 satisfy the inequalities $|a_1| \gg |a_m|$ and $|b_1| \gg |b_m|$, where $m \geq 2$, the polarizabilities of the particle are dominated by the first electric and magnetic components. In this case, only those terms with a_1 and b_1 need to be kept, and all other terms can be neglected. The electric and magnetic moments can be presented as $\vec{p} = \alpha_e \vec{E}$ and $\vec{m} = \alpha_m \vec{B}$, respectively. Here $\vec{E}$ and $\vec{B}$ are the incident electric and magnetic fields, respectively. The two polarizabilities are

$$\alpha_e = \frac{3i}{2k^3}\varepsilon a_1 = \alpha_e^{(0)}\left(1 - i\frac{2}{3\varepsilon}k^3\alpha_e^{(0)}\right)^{-1}, \text{ where } \alpha_e^{(0)} = \varepsilon r^3 \frac{\varepsilon_p - \varepsilon}{\varepsilon_p + 2\varepsilon}$$

$$\alpha_m = \frac{3i}{2k^3}\frac{b_1}{\mu} = \alpha_m^{(0)}\left(1 - i\frac{2}{3}\mu k^3\alpha_m^{(0)}\right)^{-1}, \text{ where } \alpha_m^{(0)} = \frac{r^3}{\mu}\frac{\mu_p - \mu}{\mu_p + 2\mu}$$

Here μ_p and μ are the magnetic permeability, and ε_p and ε are the electric permittivity of the particle and of the surrounding medium, respectively. Considering the small particle as an electric dipole subjected to the Lorentz force in an incident electromagnetic field, one can obtain the relation

$$\vec{F} = \frac{\alpha_e'}{4}\nabla|\vec{E}|^2 + \frac{k}{2\sqrt{\varepsilon}}\alpha_e''\mathrm{Re}\left[\vec{E} \times \vec{B}^*\right] + \frac{\alpha_e''}{2}\mathrm{Im}\left[(\vec{E}^* \cdot \nabla)\vec{E}\right]$$

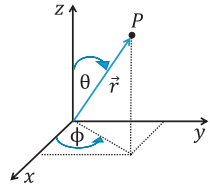
where $\alpha_e = \alpha_e' + i\alpha_e''$. The *first term* is the **gradient force**, the *second term* is the **scattering force** or **radiation pressure**, and the *third term* is the **spin–curl optical force**, which is much smaller than the gradient and scattering forces.

Equation Summary

❖ **Spherical coordinates** or **spherical polar coordinates** contain:

- ✓ the length r of the radius vector $\vec{r}$ of the point P
- ✓ the angle θ between the z axis and the radius vector $\vec{r}$
- ✓ the angle ϕ between the x axis and the projection of the radius vector $\vec{r}$ on the xy plane

With the values $0 \leq r \leq \infty$, $0 \leq \theta \leq \pi$, and $-\pi \leq \phi \leq \pi$, every point of space can be described.



The transition formulas between Cartesian coordinates and spherical polar coordinates are

$$x = r \cdot \sin\theta \cdot \cos\phi,\ y = r \cdot \sin\theta \cdot \sin\phi,\ z = r \cdot \cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2},\ \theta = \arctan\frac{\sqrt{x^2 + y^2}}{z},\ \phi = \arctan\frac{y}{x}$$

❖ The **nabla operator** ∇ is a symbolic vector. In Cartesian coordinates, it is defined as

$$\nabla = \frac{\partial}{\partial x}\vec{i} + \frac{\partial}{\partial y}\vec{j} + \frac{\partial}{\partial z}\vec{k}$$

❖ The **Laplace operator** prescribes the summation of the second partial derivatives. In spherical coordinates, it is written as

$$\Delta = \nabla \cdot \nabla = \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Here

$$\nabla^2_{\theta,\phi} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

denotes the θ and ϕ parts of the Laplace operator in spherical coordinates.

Equation Summary

In Cartesian coordinates, the Laplace operator has the form

$$\Delta = \nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- The **divergence** of a vector field is

$$\nabla \cdot \vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$$

- The **curl** of a vector field is

$$\nabla \times \vec{A} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix} = \vec{i}\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right) + \vec{j}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right) + \vec{k}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)$$

- The **Legendre polynomials** can be defined using Rodrigues' formula as

$$P_l^m(x) = \frac{1}{2^n n!}(1-x^2)^{m/2}\frac{d^{l+m}(x^2-1)^l}{dx^{l+m}}$$

The first nine of these functions are as follows:

$$P_0^0(x) = 1$$

$$P_1^0(x) = x$$

$$P_1^1(x) = (1-x^2)^{1/2}$$

$$P_1^{-1}(x) = -\frac{1}{2}(1-x^2)^{1/2}$$

$$P_2^0(x) = \frac{1}{2}(3x^2-1)$$

$$P_2^1(x) = 3x(1-x^2)^{1/2}$$

$$P_2^{-1}(x) = -\frac{1}{2}x(1-x^2)^{1/2}$$

$$P_2^2(x) = 3(1-x^2)$$

$$P_2^{-2}(x) = \frac{1}{8}(1-x^2)$$

Equation Summary

❖ The **associated Laguerre polynomial** can be generated by the following equation:

$$L_{n+l}^{2l+1}(x) = \left(\frac{d}{dx}\right)^{2l+1}\left[e^{x}\left(\frac{d}{dx}\right)^{n+l}(x^{n+l}e^{-x})\right]$$

The first four of these functions are

$$L_1^1(x) = 1,\ L_2^1(x) = 2x - 4,\ L_2^2(x) = 2,\ L_3^3(x) = -6$$

❖ The **Lorentzian function** (the **Lorentz** or **Breit–Wigner curve**) can be obtained from the damped oscillation described by the function

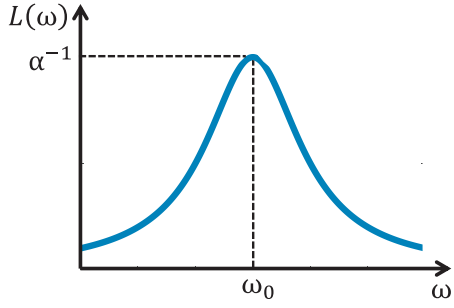
$$f(t) = \mathrm{Re}[f^*(t)] = \begin{cases} 0 & t < 0 \\ e^{-\alpha t}\cos\omega_0 t & t \geq 0 \end{cases}$$

$$\text{where } f^*(t) = \begin{cases} 0 & t < 0 \\ e^{(-\alpha+i\omega_0)t} & t \geq 0 \end{cases}$$

The Fourier transform of the damped oscillation is the **Lorentzian** or **Breit–Wigner curve**:

$$\mathcal{F}\{f^*(t)\} = \int_0^\infty e^{-i\omega t}e^{(-\alpha+i\omega_0)t}dt = \frac{e^{-\alpha t}e^{i(\omega-\omega_0)t}}{-\alpha + i(\omega_0 - \omega)}\Bigg|_0^\infty =$$

$$= \frac{\alpha + i(\omega_0 - \omega)}{\alpha^2 + (\omega - \omega_0)^2} \Rightarrow \boxed{L(\omega) = \mathcal{F}\{f(t)\} = \frac{\alpha}{\alpha^2 + (\omega - \omega_0)^2}}$$



Equation Summary

- A **Gaussian function** (or a **Gaussian**) is a function of the form

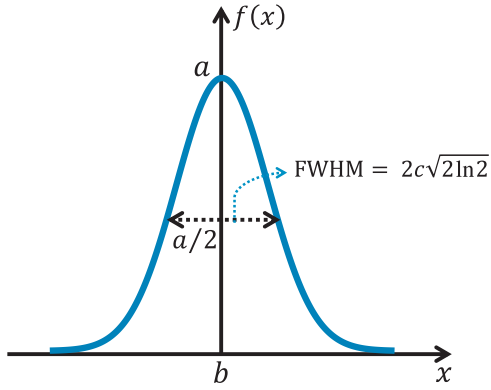
$$f(x) = ae^{-\frac{(x-b)^2}{2c^2}}$$

where a, b, and $c \neq 0$ are arbitrary real constants.

- If a function $f(x)$ has all derivatives at $x = a$, it can be represented in an interval about $x = a$ as a power series:

$$f(x) = \sum_k^{\infty} \frac{f^{(k)}(a)}{k!}(x-a)^k \text{ (Taylor series)}$$

$$f(x) = \sum_k^{\infty} \frac{f^{(k)}(0)}{k!}x^k \text{ (Maclaurin series)}$$



The full width at half maximum (FWHM) is

$$\text{FWHM} = 2c\sqrt{2\ln 2}$$

The integral of the Gaussian function is

$$\int_{-\infty}^{+\infty} ae^{-\frac{(x-b)^2}{2c^2}}dx = a\sqrt{2\pi c^2}$$

Equation Summary

- In **Fermi–Dirac statistics**, the probability that a state of energy E is occupied by a fermion is

$$N(E) = \left[1 + \exp\left(\frac{E - \mu}{\kappa_B T}\right)\right]^{-1}$$

In the case of Fermi–Dirac distribution, the chemical potential μ is called the **Fermi energy** E_F. At $T = 0$ K, fermions fill all energy states below a level E_F, with one and only one particle per a state. For $T > 0$ K, some fermions are elevated to levels above E_F.

- A **Boltzmann distribution** gives the probability of finding a system in a certain state as a function of the energy of this state and the thermodynamic temperature T of the system. This probability is written as

$$p_i = \frac{e^{-E_i/\kappa_B T}}{Z}, \text{where } Z = \sum_{j=1}^{M} e^{-E_j/\kappa_B T}$$

p_i is the probability of finding the system in the state i, E_i is the energy of state i, κ_B is the **Boltzmann constant**, M is the number of states accessible to the system of interest, and Z is known as the **canonical partition function**, which serves as the normalization constant and results from the statement that the sum of probabilities of all states must be equal to unity. The ratio of the two probabilities is

$$\frac{p_i}{p_j} = e^{(E_j - E_i)/\kappa_B T}$$

- A **thermal average** of value A is $\langle A \rangle = \frac{\sum_n A e^{(-E_n/\kappa_B T)}}{\sum_n e^{(-E_n/\kappa_B T)}}$ where E_n is the energy of the n^{th} excited state of the quantum mechanical oscillator.

- A **tensor of rank *n*** $\mathbf{T}$ in a Cartesian coordinate system K is a physical quantity that can be described by 3^n elements $t_{ij\ldots m}$, the so-called translation invariants. Here the number of indices $i, j, \ldots, m$ exactly equals n ($n > 0$). The indices are ordered, and every one of them takes the values 1, 2, and 3.

Equation Summary

A coordinate transformation from K to $\tilde{K}$ must satisfy the relation

$$\tilde{t}_{\mu\nu\ldots\rho} = \sum_{i=1}^{3}\sum_{j=1}^{3}\cdots\sum_{m=1}^{3} a_{\mu i}a_{\nu j}\ldots a_{\rho m}t_{ij\ldots m}$$

where the elements $t_{ij\ldots m}$ with ordered indices are the **components of the tensor** $\mathbf{T}$.

For example:

✓ A tensor of rank 1 is a vector. It has three components: t_1, t_2, and t_3. The transformation law is given as

$$\tilde{t}_\mu = \sum_{i=1}^{3} a_{\mu i}t_i, \text{ where } \mu = 1,\ 2,\ 3$$

✓ A tensor of rank 2 is a matrix. It has nine components t_{ij}, which can be arranged as

$$\mathbf{T} = T = \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{pmatrix}$$

The transformation has the form

$$\tilde{t}_{\mu\nu} = \sum_{i=1}^{3}\sum_{j=1}^{3} a_{\mu i}a_{\nu j}t_{ij}, \text{ where } \mu,\ \nu = 1,\ 2,\ 3$$

❖ The symbol δ_{ij} is the **Kronecker symbol**:

$$\delta_{ij} = \begin{cases} 1, & \text{for } i = j \\ 0, & \text{for } i \neq j \end{cases}$$

❖ Scattering of electromagnetic waves by a dielectric sphere can be described using **vector spherical harmonics**.

Equation Summary

A time-harmonic electromagnetic field $(\vec{E}, \vec{H})$ in a linear, isotropic, homogeneous medium satisfies the wave equations,

$$\nabla^2 \vec{E} + k^2 \vec{E} = 0 \quad \text{and} \quad \nabla^2 \vec{H} + k^2 \vec{H} = 0$$

where $k^2 = \omega^2 \varepsilon \mu$. Their solutions are not straightforward since $\vec{E}$ and $\vec{H}$ must satisfy the following conditions:

✓ $\vec{E}$ and $\vec{H}$ are divergence free, i.e.,

$$\nabla \cdot \vec{E} = 0 \quad \text{and} \quad \nabla \cdot \vec{H} = 0$$

✓ $\vec{E}$ and $\vec{H}$ are related according to

$$\nabla \times \vec{E} = i\omega\mu \vec{H} \quad \text{and} \quad \nabla \times \vec{H} = -i\omega\varepsilon \vec{E}$$

We construct a vector function as

$$\vec{M} = \nabla \times (\vec{c}\psi)$$

where $\vec{c}$ is an arbitrary constant vector, and ψ is a scalar function. $\vec{M}$ is divergence free, i.e.,

$$\nabla \cdot \vec{M} = 0$$

If we apply the operator $\nabla^2 + k^2$ to $\vec{M}$, we obtain

$$\nabla^2 \vec{M} + k^2 \vec{M} = \nabla \times [\vec{c}(\nabla^2 \psi + k^2 \psi)]$$

$\vec{M}$ satisfies the *vector* wave equation if ψ is a solution to the *scalar* wave equation,

$$\nabla^2 \psi + k^2 \psi = 0$$

If this condition and the previous ones are satisfied, $\vec{M}$ is equivalent to the electric or magnetic field.

We construct another divergence-free vector function:

$$\vec{N} = \frac{\nabla \times \vec{M}}{k} \quad \text{or} \quad \nabla \times \vec{N} = k\vec{M}$$

Equation Summary

$\vec{M}$ and $\vec{N}$ have all of the properties of the EM field.

The scalar function ψ is called a **generating function** for the **vector harmonics** $\vec{M}$ and $\vec{N}$; the vector $\vec{c}$ is sometimes called the **guiding** or **pilot vector**.

Considering scattering by a sphere, we choose functions ψ that satisfy the wave equation in spherical polar coordinates $\vec{r}$, θ, ϕ. If we take $\vec{c} = \vec{r}$, where $\vec{r}$ is the radius vector, then

$$\vec{M} = \nabla \times (\vec{r}\psi)$$

is a solution to the vector wave equation in *spherical polar coordinates*.

Generating functions that satisfy the scalar wave equation in spherical polar coordinates have the form

$$\psi_{emn} = \cos(m\phi) P_n^m(\cos\theta) z_n(kr)$$

$$\psi_{omn} = \sin(m\phi) P_n^m(\cos\theta) z_n(kr)$$

where z_n is any of the spherical Bessel functions j_n, y_n, or any of the spherical Hankel functions $h_n^{(1)}$, $h_n^{(2)}$. The vector spherical harmonics generated by ψ_{emn} and ψ_{omn} are

$$\vec{M}_{emn} = \nabla \times (\vec{r}\psi_{emn}), \quad \vec{M}_{omn} = \nabla \times (\vec{r}\psi_{omn})$$

$$\vec{N}_{emn} = \frac{\nabla \times \vec{M}_{emn}}{k}, \qquad \vec{N}_{omn} = \frac{\nabla \times \vec{M}_{omn}}{k}$$

The electromagnetic field scattered by a dielectric sphere can be presented as

$$\vec{E}_s = \sum_{n=1}^{\infty} E_n \left(i a_n \vec{N}_{e1n}^{(3)} - b_n \vec{M}_{o1n}^{(3)} \right)$$

$$\vec{H}_s = \frac{k}{\omega\mu} \sum_{n=1}^{\infty} E_n \left(i b_n \vec{N}_{o1n}^{(3)} + a_n \vec{M}_{e1n}^{(3)} \right)$$

Here $E_n = E_0 i^n \frac{(2n+1)}{n(n+1)}$, where E_0 is the amplitude of the incident electric field. a_n and b_n are the scattering coefficients. The superscript (3) indicates vector spherical harmonics for which the radial dependence of the generating functions is specified by $h_n^{(1)}$.

Asymptotically, the **spherical Hankel functions** $h_n^{(1)}$ can be presented as

$$h_n^{(1)} \sim \frac{(-i)^n e^{ikr}}{ikr}, \text{ where } kr \gg n^2$$

This corresponds to an outgoing spherical wave.

❖ **Optical path length** (OPL) is the product of the physical path length L traveled by light and the refractive index of the medium through which this light propagates.

✓ In a medium of constant refractive index n

$$\text{OPL} = nL$$

✓ If the refractive index changes along the physical path length,

$$\text{OPL} = \int_L n(l)dl$$

where $n(l)$ is the local refractive index along the physical path L.

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Light–Matter Interaction

Galina Nemova

Our understanding of the interaction of light and matter has a long history that has evolved from the ancient corpuscular theory to the wave theory and, finally, to the quantum theory. Matter is composed of charged particles, and among these particles are positively charged nuclei surrounded by electrons that are in motion. Light is an oscillating electromagnetic wave. But light is also particles (photons). The primary objective of this Field Guide is to provide the basic principles of light–matter interaction using classical, semiclassical, and quantum theories. To this end, the guide provides the formulae for, and descriptions of, phenomena that are fundamental to our current state of knowledge of light–matter interaction.

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